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(10)

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FOREWORD

This report was prepared by Wyandotte Chemicals Corporation and University of Illinois under USAF Contract No. AF 33(616)-7214. This contract was initiated under Project 7340, "Nonmetallic and Composite Materials," Task No. 734007, "Coatings for Energy Utilization, Control and Protective Functions." The work was administered under the direction of Nonmetallic Materials Laboratory, Directorate of Materials and Processes, Aeronautical Systems Division, with technical guidance on behalf of Aeronautical Systems Division furnished by Mr. J. J. Mattice, Project Engineer.

This report covers work conducted from April 1962 to January 1963.

The work at Wyandotte Chemicals Corporation was performed by Dr. R. L. Schaefer, Senior Research Chemist, with assistance by Mr. R. L. Thivierge. This report includes work performed under subcontract to University of Illinois (Account No. 44-32-19-394) by Dr. K. L. Rinehart, Jr., principal investigator and Dr. D. E. Bublitz.

Work reported under Section I was performed at Wyandotte Chemicals Corporation; that under Section II was performed at University of Illinois.

ABSTRACT

SECTION I.

In a search for metallocene derivatives as additives, monomers, and polymers with high ultraviolet radiation resistance, the preparation of osmocene and ruthenocene analogs of *o*-hydroxybenzophenone was investigated, and a study was made of the conversion of functional cyclopentadienes to ferrocenes. Urethanes prepared from 1,1'-ferrocenediisocyanate were not unusually stable. New compounds prepared included *o*-hydroxybenzoylosmocene, *o*-hydroxybenzoylruthenocene, *o*-methoxybenzoylruthenocene, 1,1'-bis(~~beta~~ ^{beta}-diethoxyethyl)-ferrocene, 1,1'-bis(~~beta~~ ^{beta}-hydroxyethyl)-ferrocene, $[(C_5H_5O)_2CHCH_2C_6H_4]_3Hf$, $(HOCH_2CH_2C_6H_4)_4H_2Fe$, dimethyl and diethyl 1,1'-ferrocene-dicarbamates, poly(1,1'-ferrocenedimethyl 1,1'-ferrocenedicarbamate), Os_2OCl_8 , 6-carbethoxy-3,4-dihydrofulvene, and cyclopentadienes containing *beta*-carbethoxyethyl, cyanomethyl, *beta*-diethoxyethyl, and *beta*-hydroxyethyl groups.

SECTION II.

Isomeric bis- and tris-(trimethylene)ferrocenes were prepared and acetylated. The acetyl products were converted to the corresponding ferrocene-propionic acids, which on cyclization were shown to give homoannular ketonic products, as well as the expected heteroannular compounds.

This technical documentary report has been reviewed and is approved.

* *beta*

x x UV



J. M. Kelble, Chief
Elastomers and Coatings Branch
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SECTION I

I. INTRODUCTION

The purpose of this program was the synthesis of metal cyclopentadienyl compounds for use as novel and improved additives, monomers, and polymers possessing high ultraviolet radiation resistance.

The need for ferrocene derivatives for testing as ultraviolet absorbers for protection of plastics and coatings from photochemical degradation led to the synthesis of twelve α -carbonyl-substituted ferrocenes, including analogs of commercial absorbers, as described in Part I of this report (1). From a continuation of this work and expansion into the area of difunctional ferrocenes for eventual preparation of polymers, eleven ferrocenes with a variety of functional groups were obtained, primarily by Friedel-Crafts reactions on ferrocene and by reactions on 1,1'-ferrocenedicarboxylic acid. In addition, samples of osmocene and benzoylosmocene were prepared (2).

In the work described below, emphasis was placed on the preparation of difunctional ferrocenes from cyclopentadiene derivatives and on the synthesis of osmocene and ruthenocene analogs of o-hydroxybenzophenone.

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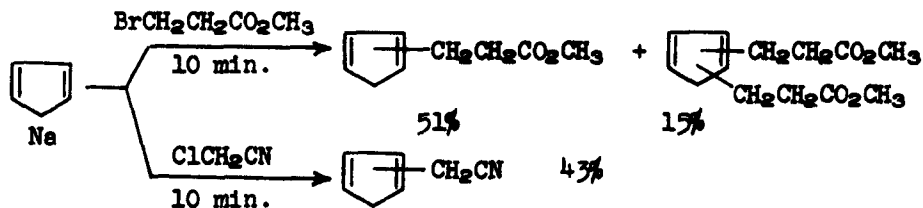
II. DISCUSSION

A. Ferrocenes from Cyclopentadiene

In an effort to obtain difunctional ferrocenes for incorporation into polymers, cyclopentadienyllithium or cyclopentadienylsodium was treated with epoxides or with alkyl halides containing functional groups, and the substituted cyclopentadienes that were isolated were subjected to sandwiching conditions. The following reactants were employed: methyl 3-bromopropionate, chloroacetonitrile, chloroacetaldehyde diethyl acetal, ethyl chloroacetate, ethylene dichloride, epichlorohydrin, and ethylene oxide. In addition, benzyl chloride was used to prepare benzylcyclopentadiene as a potential precursor to dibenzoylosmocene.

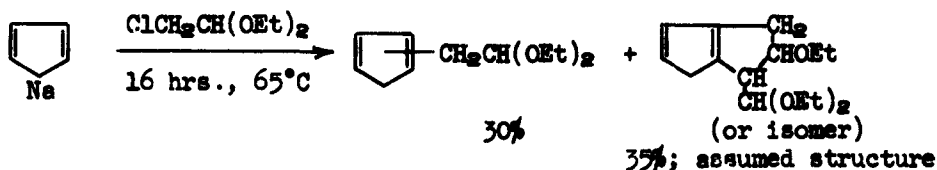
Although reactions of alkali metal derivatives of cyclopentadiene with alkyl halides to form alkylcyclopentadienes have been known for some time (3), the preparation of cyclopentadienes containing reactive functional groups by this method has apparently been limited to the reaction with epichlorohydrin (4). The possibility existed, of course, that with alkyl halides containing ester, nitrile, or acetal linkages, reaction would occur at the functional group in competition with that at the halo group.

Addition of methyl 3-bromopropionate to cyclopentadienylsodium in tetrahydrofuran in a -70°C bath under nitrogen and workup shortly after the exotherm was complete yielded 51% β -carbomethoxyethylcyclopentadiene and 15% bis(β -carbomethoxyethyl)-cyclopentadiene.* Similarly, (cyanomethyl)-cyclopentadiene was obtained from chloroacetonitrile in 43% yield, but in this case no bis compound could be isolated, although there was considerable distillation residue.

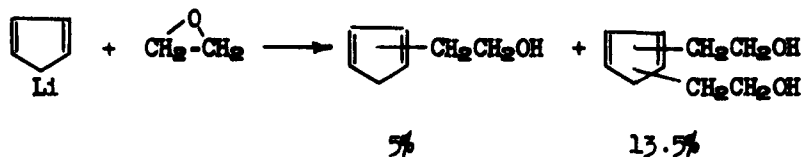


* Throughout this report compounds containing a substituted cyclopentadiene ring are referred to without designation of the relative positions of substituents and double bonds in the ring. In the monosubstituted compounds, the position of attachment is not critical to the investigation, inasmuch as the final products prepared from the cyclopentadiene compounds are ferrocenes, in which the ring positions are equivalent.

A mixture of cyclopentadienylsodium and chloroacetaldehyde diethyl acetal in tetrahydrofuran refluxed several hours furnished 30% β,β -diethoxyethylcyclopentadiene. Despite the lengthy heating period, the product had not dimerized but distilled at pot temperatures well below the usual depolymerization temperatures of cyclopentadienes.* In addition to this compound, a wide-boiling mixture of cyclopentadienes was obtained, elemental analyses on which were consistent with a bis(β,β -diethoxyethyl)-cyclopentadiene from which ethanol had split out (i.e., $C_{15}H_{24}O_3$). It is interesting to note that reactions of phenyllithium and butyllithium in ether with chloroacetaldehyde diethyl acetal failed to yield the desired acetals (6).



Treatment of a mixture of cyclopentadienyllithium and cyclopentadiene in tetrahydrofuran with excess ethylene oxide and workup 1 hr. after the exotherm began near 40°C yielded 5% β -hydroxyethylcyclopentadiene and 13.5% bis(β -hydroxyethyl)-cyclopentadiene. An earlier run had given similar results (2). When essentially no free cyclopentadiene was present, the yield of β -hydroxyethylcyclopentadiene was negligible. The reaction of cyclopentadienylsodium with ethylene oxide during 0.5-hr. reflux in ether was described by Boberg and Schultze, who obtained dimeric β -hydroxyethylcyclopentadiene in 12.5% yield (7).

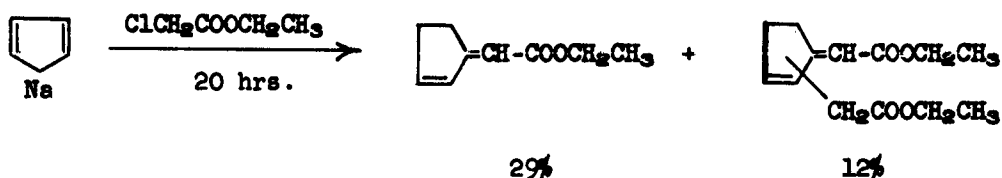


That the above mentioned cyclopentadiene compounds did indeed contain the cyclopentadiene ring was shown by ultraviolet and infrared spectra. All the cyclopentadienes showed strong absorption in the ultraviolet at 2440-2490 Å (Table 1), as would be expected of "alkyl" cyclopentadienes (cyclopentadiene λ_{max} 2380 Å; a 1-methyl group contributes 70 Å (8)). In addition, all

* A complication encountered with most work on cyclopentadiene compounds is the tendency of cyclopentadienes to self-condense in Diels-Alder fashion to give dimers and higher polymers. However, depolymerization to the monomers above 150°C can sometimes be accomplished even with dicyclopentadienes containing functional groups (5).

showed strong absorption in the infrared at 11-11.3 μ ,* a region known to be characteristic of a double bond in a cyclopentyl ring (9). Strong bands in this region readily differentiated the monomers from the dimers, which showed weak absorption at most, in the three cases examined [dicyclopentadiene, di(β -hydroxyethylcyclopentadiene), and di(cyanomethylcyclopentadiene)].

When a mixture of cyclopentadienylsodium and ethyl chloroacetate in tetrahydrofuran was stirred 20 hrs., the two products isolated showed maximum absorption in the ultraviolet at 2680 Å, well above the maxima of the cyclopentadienes but coincident with the region for dienes conjugated with a carbonyl group (8). Evidently, double-bond migration occurred to give 6-carbethoxy-3,4-dihydrofulvene (29%) and carbethoxymethyl-6-carbethoxy-3,4-dihydrofulvene (12%). Although the infrared spectrum supported the doubly-conjugated-ester structure (strong bands at 5.94, 6.24, 8.36, and 8.93 μ), a medium carbonyl band at 5.85 μ indicated the presence of a small amount of a singly-conjugated ester, presumably ethyl 3-cyclopentenylideneacetate.

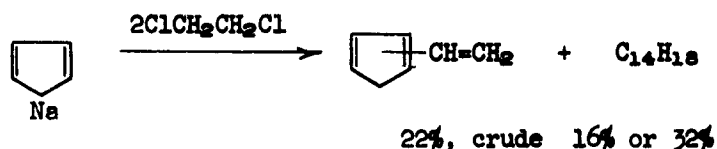


Benzylcyclopentadiene was described prepared from benzyl chloride and the potassium (3) and sodium (10) derivatives of cyclopentadiene, but yields were not reported. We have prepared it in 46-47% yields from the sodium and lithium derivatives. No attempt was made to isolate the by-product (3) dibenzylcyclopentadiene.

From a reaction between cyclopentadienylsodium and a 100% excess of ethylene dichloride, two impure hydrocarbons were obtained. One of the hydrocarbons ($\text{C}_{14}\text{H}_{18}$, ca.) was not a cyclopentadiene and was not further investigated. Comparison of the ultraviolet maximum of the other hydrocarbon with that of a product from a related reaction indicated that the material was vinylcyclopentadiene (22%; λ_{max} 2550 Å, $\log \epsilon$ 4.00). Analyses were in agreement provided the material was assumed to contain about 8% ethylene dichloride. Thus, the reaction of epichlorohydrin and cyclopentadienylsodium

* The absorption for bis (β -carbomethoxyethyl)-cyclopentadiene was medium-weak. Inasmuch as the $\log \epsilon$ value of the ultraviolet absorption maximum at 2460 Å was also significantly less than that for the mono compound, the material may have contained a non-cyclopentadienyl impurity (e.g., the adduct of methyl acrylate and the mono compound).

was recently reported to give not α -hydroxymethyl- β -chloromethylcyclopentadiene but the dehydrochlorinated product α -hydroxymethyl-vinylcyclopentadiene (64%; λ_{\max} 2580 Å, $\log \epsilon$ 3.38) (4). Before this reaction was reported, we attempted a similar reaction from cyclopentadienyllithium, but no pure products were isolated.



The preparation of difunctional ferrocenes from monofunctional cyclopentadienyl intermediates has been described in a number of publications, as noted in Part II of this report (2). Thus, in particular instances sandwiching has been successful in the presence of the following groups: carbomethoxy (11), acetyl (11) (12), diethylaminoalkyl (13), phenylazo (14), methyldiethoxysilyl (15), piperidinodimethylsilyl (15), hexamethyldisiloxanyl (16), and the sodium salt of an alcohol (17).

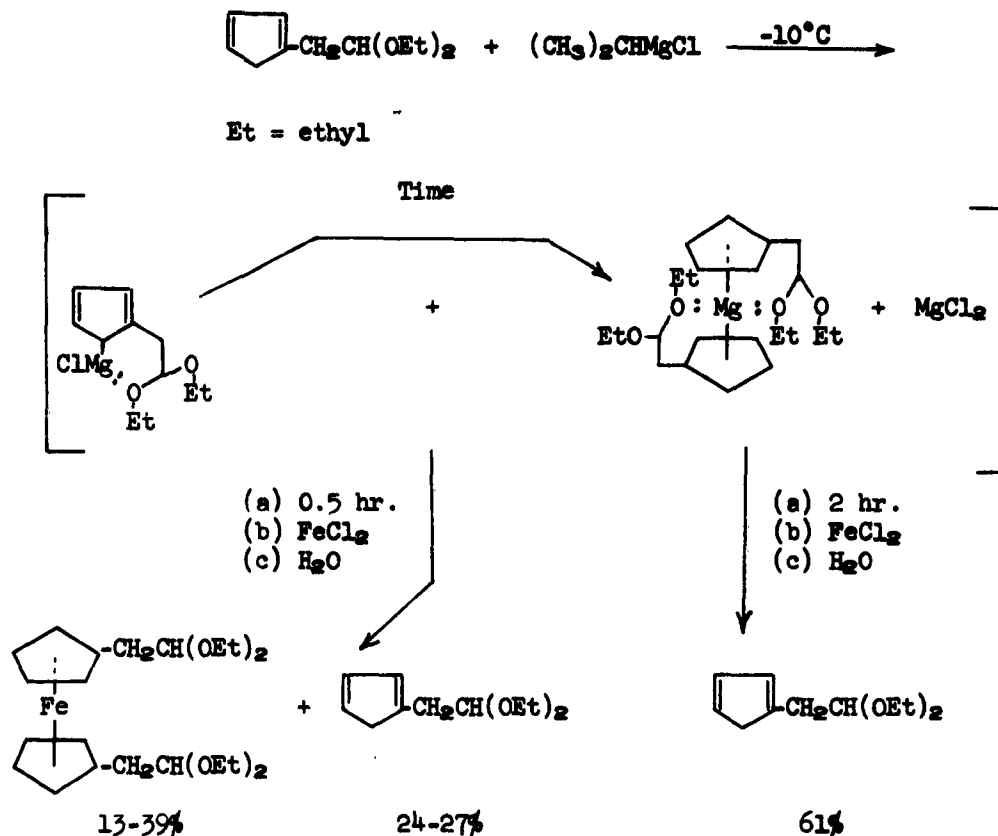
Treatment of β,β -diethoxyethylcyclopentadiene in tetrahydrofuran with isopropylmagnesium chloride at -10° followed 0.5-hr. later by ferrous chloride yielded 13-39% 1,1'-bis(β,β -diethoxyethyl)-ferrocene and returned 24-27% of the starting acetal. When the isopropylmagnesium chloride and acetal were in contact for 2 hrs. instead of 0.5 hr. before addition of ferrous chloride, 61% of the starting acetal was recovered. This peculiar result, in which it appeared that the longer the reactants were in contact the more starting material was recovered, may be explained simply by assuming that the "Schlenk equilibrium" (18) led to an unreactive (to FeCl_2) bis(cyclopentadienyl)-magnesium derivative coordinated by ether oxygens from the two attached acetal groups.* (See Reaction Scheme 1.)

In addition to the ferrocene, another iron-containing compound was isolated from the reaction in 2% yield as a sharp chromatographic fraction. Elemental analyses indicated that there were three β,β -diethoxyethylcyclopentadienyl units (+ H) per iron atom. The ultraviolet and visible spectra showed much stronger absorption than that of ferrocene (Figure 1). To account for the increased absorption, the compound must have been either a ferrocene with a strongly absorbing substituent or else a non-ferrocene with an electronic system that absorbed more strongly than ferrocene.



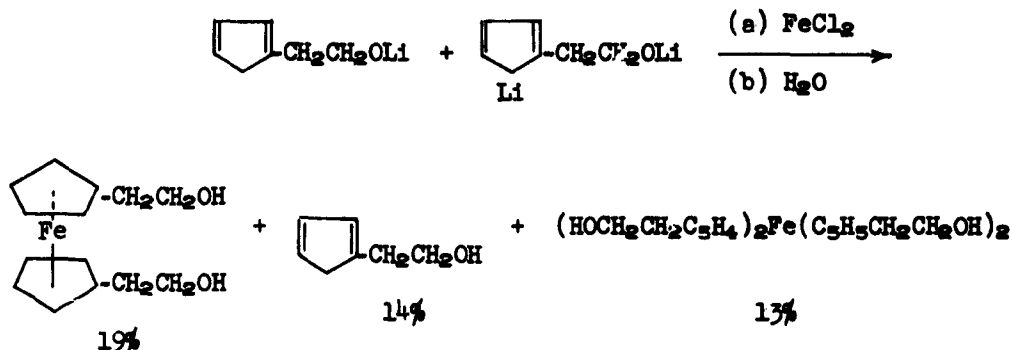
* Evidence has been presented that bis(cyclopentadienyl)-magnesium has a sandwich structure (19).

REACTION SCHEME 1



When β -hydroxyethylcyclopentadiene was subjected to sandwiching conditions, a compound containing four β -hydroxyethylcyclopentadienyl units ($\pm 2-4$ H) per iron atom was isolated along with the ferrocene compound. Thus, addition of butyllithium to β -hydroxyethylcyclopentadiene at a 1.4-to 1 molar ratio yielded 19% 1,1'-bis(β -hydroxyethyl)-ferrocene and 13% $(C_5H_4CH_2CH_2OH)_4Fe$, and returned 14% of the starting cyclopentadiene. The ultraviolet and visible spectra of the latter iron compound (Figure 1) closely resembled that of the above tri-compound, and again the absorption was too strong to be that of an alkylferrocene. In a single experiment, hydrogenation of an ethanol solution of the tetra-compound with palladium on charcoal as catalyst at 25°C did not change the ultraviolet spectrum of the solution. This would suggest that all the double bonds are either coordinated to iron or form part of an aromatic system not readily hydrogenated. Although the actual structures remain in question, the data suggest that the tetra-compound, $C_{28}H_{38}FeO_4$, is bis(β -hydroxyethylcyclopentadienyl)-iron bis(β -hydroxyethylcyclopentadiene). By

analogy, the tri-compound, $C_{33}H_{52}FeO_3$, would be β,β -diethoxyethylcyclopentadienyliron bis(β,β -diethoxyethylcyclopentadiene), which bears a formal resemblance to the known π - $C_5H_5Fe(CO_2)-\sigma$ - C_5H_5 (10). Heretofore, compounds containing more than two cyclopentadiene rings bound to iron have not been described.



Another "tetra-compound" was isolated when the compound $C_{15}H_{24}O_3$ obtained from cyclopentadienylsodium and chloroacetaldehyde diethyl acetal was treated with isopropylmagnesium chloride and ferrous chloride. The reaction yielded 3% $(C_{15}H_{22}O_3)_4H_2Fe$ and a larger amount of crude ferrocene $(C_{15}H_{23}O_3)_2Fe$, and returned 62% of the starting material.

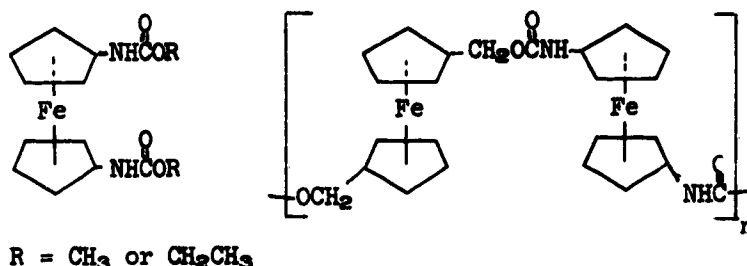
Benzylcyclopentadiene treated with methyllithium and ferrous chloride furnished 45-72% 1,1'-dibenzylferrocene. Although sodium dispersion also reacted with benzylcyclopentadiene, addition of ferrous chloride did not give a practical amount of dibenzylferrocene. Sodium dispersion has been used to prepare sodium derivatives of cyclopentadiene (11), but it is also known to add to dienes to give disodio derivatives (20). Dibenzylferrocene was previously prepared from benzylcyclopentadiene in undisclosed yield (10) (12).

Attempts to convert (cyanomethyl)-cyclopentadiene or bis(β -hydroxyethyl)-cyclopentadiene to ferrocenes were unsuccessful. A similar attempt with β -carbomethoxyethylcyclopentadiene also failed, but recent examination of the proportions of reagents employed showed a considerable excess of metalating agent, and the experiment was therefore meaningless. The product from the reaction of cyclopentadienylsodium and ethyl chloroacetate was also subjected to sandwiching conditions before it was established that the compound was a dihydrofulvene and not a cyclopentadiene; no ferrocenes were isolated.

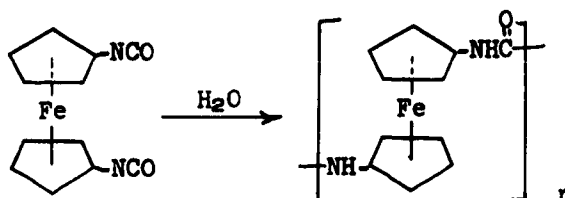
B. Urethanes from 1,1'-Ferrocene Diisocyanate

In order to determine if urethanes prepared from 1,1'-ferrocene diisocyanate show unusual thermal stability, the diisocyanate was treated with methanol, ethanol, and with 1,1'-di(hydroxymethyl)-ferrocene to give the

urethanes. Differential thermal analysis data indicated that the urethanes began to decompose in the range 245-280°C. The reaction with 1,1'-di(hydroxymethyl)ferrocene yielded a soluble polyurethane when tetrahydrofuran was the reaction medium, but when benzene was used, the product was insoluble in tetrahydrofuran and other common solvents.



The diisocyanate was also hydrolyzed in an effort to obtain diaminoferrocene, but elemental analyses and infrared data indicated that the insoluble product was either 1,1'-ferrocenylenurea or poly(ferrocenylenurea) (61%).



C. Miscellaneous Reactions on Ferrocene

Results from modification of an earlier procedure (21) for preparation of diferrocenylmethanol in 20% yield indicated that a simple procedure could be developed, although the present one was not ideal (18% yield, or 40% based on recovered ferrocene).

An attempted Friedel-Crafts reaction on ferrocene with chloroacetaldehyde diethyl acetal and aluminum chloride caused 37% oxidation to ferricinium ion. In addition, oxidation of ferrocene-products amounted to 23% (as ferrocene). Some ferrocene (19%) was recovered, and a low-melting solid (15%, ca.) was obtained in crude form. An explanation for this oxidation would follow lines similar to that given for ferrocene oxidation encountered with mixtures of aluminum chloride and acyl chlorides having electron-withdrawing groups adjacent to the chlorocarbonyl group (2).

Treatment of lithiated ferrocene with acetaldehyde and with epichlorohydrin followed by hydrolysis gave 57% and 83% recovered ferrocene, respectively. Apparently, significant trans-metalation occurred. With benzaldehyde, the

ferrocenyl-alcohols produced could not be readily separated from the larger quantity of butylphenylcarbinol, which formed from the excess of butyllithium. Recovery of crude ferrocene was 30%, which is normal for reactions on lithiated ferrocene. Had this reaction succeeded, it would have been applied to lithiated osmocene (22) in an effort to obtain a precursor to 1,1'-dibenzoylosmocene, which is not accessible by a Friedel-Crafts reaction (22).

Reduction of chloroacetylferrocene with sodium borohydride in isopropyl alcohol as described for reduction of diacetylferrocene to di(hydroxyethyl)-ferrocene (23) gave a crude alcohol, m.p. 56-66°C, which could not be readily purified. When 1,2-dimethoxyethane was the solvent, chromatographic fractions were oils.

D. New Organoiron Complexes (Unsuccessful)

The isolation of compounds containing three and four substituted cyclopentadiene rings per iron atom as described above suggested that it might be possible to form iron complexes from the reactions of other olefins with organo-metallic compounds and ferrous chloride. This area was briefly examined without success.

Thus, butadiene and ferrous chloride were added to ethylmagnesium chloride in ether-tetrahydrofuran below -50°C, the temperature allowed to rise, and after several hours the mixture was hydrolyzed with dilute acid. The iron-containing fraction, which was obtained in very low yield, showed significant hydroxyl absorption in the infrared and was relatively polar. It was not further investigated. The use of 4-methoxybutylmagnesium chloride in place of ethylmagnesium chloride yielded two small colored fractions, but tests for iron were very weak. Ferrous chloride was also added to allylmagnesium chloride at a 1 to 4 molar ratio. Again the only highly colored fraction obtained (in low yield) after hydrolysis and chromatography was a polar material.

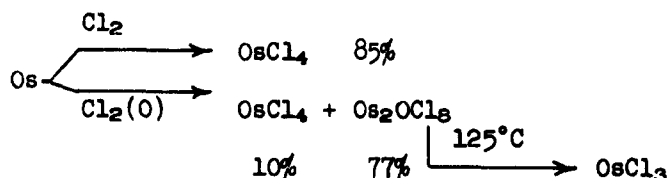
The data obtained with substituted cyclopentadienes as starting materials also suggested that an excess of unmetallated diene should be present to permit formation of the tri- and tetra-compounds. However, from treatment of a mixture of cyclopentadienyllithium and cyclopentadiene with ferrous chloride, no tri- or tetra-compounds could be isolated.

E. Osmocene Derivatives

There are certain applications for which an ultraviolet protector should be colorless or sufficiently light not to discolor the finished item. In an effort to obtain absorbers with the effectiveness of the ferrocenes but without significant absorption in the visible region, attention was given to the preparation of osmocene and its derivatives (2). Osmocene or bis(cyclopentadienyl)-osmium is the only colorless metal cyclopentadienyl known to be both

hydrolytically and thermally stable. It has been prepared by the reaction of cyclopentadienylsodium with osmium tetrachloride in 1,2-dimethoxyethane in 23% yield (24) and in tetrahydrofuran in 10% yield (25).

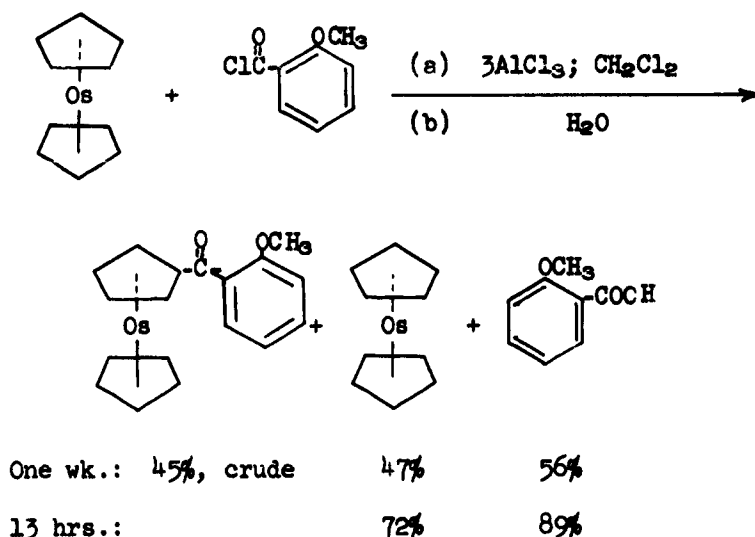
Chlorination of osmium at 650-700°C is known to give osmium tetrachloride in 50-65% yields along with a small amount of more volatile material described as a mixture of chlorides (26). When the chlorination was carried out in the present work with chlorine from a fresh cylinder, the product obtained was almost entirely volatile material, which was found to be soluble in hydrocarbons. Inasmuch as an osmium chloride readily soluble in organic solvents could be useful for synthesis of osmocene derivatives, the preparation of this material was investigated further. The chlorine proved to be contaminated with air. Bleeding air into a stream of pure chlorine at a 1 to 15 ratio during chlorination at 675-700°C yielded the soluble chloride along with 10% osmium tetrachloride. Analyses on the soluble compound were in excellent agreement for the previously unreported diosmium oxide octachloride, Os_2OCl_8 (77% yield). The material was very hygroscopic and decomposed at 125°C at 5 mm., in part to pure osmium trichloride. The only other true osmium oxychloride reported in the literature is osmium oxide tetrachloride, OsOCl_4 , prepared by treatment of osmium with an 8:1 ratio of chlorine and oxygen at 400°C (27). An oxyfluoride, OsOF_5 , was reported recently (28). In the absence of air, the chlorination yielded analytically pure osmium tetrachloride in 85% yield.



Treatment of cyclopentadienylsodium with osmium tetrachloride in 1,2-dimethoxyethane by the known procedure (24) furnished osmocene in 8, 11, 13, and 12% yields. Similarly, 0.0268 mole of diosmium oxide octachloride with 0.238 mole of cyclopentadienylsodium gave 10 and 11% yields of osmocene. Attempts were also made to prepare osmocene from two samples of commercial "osmium trichloride", but yields were very small, and examination of the starting chlorides showed that one was hydrated and the other contained a 1 to 1 ratio of oxygen to osmium. The latter at 500°C gave $(\text{Os}_2\text{Cl}_3\text{O}_2)_n$, which has not been described previously in the literature.

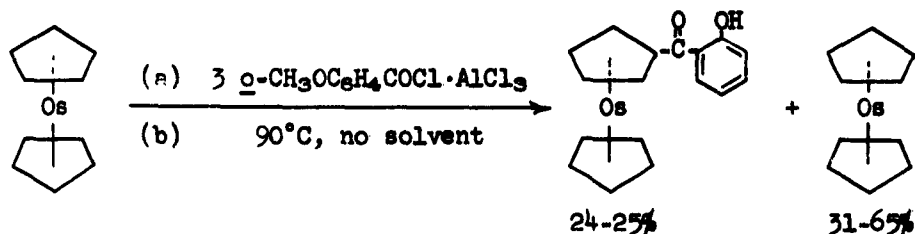
Osmocene was converted to o-methoxybenzoylosmocene to be used as a precursor to the o-hydroxy compound, which is an analog of the parent of the hydroxybenzophenone absorbers. Thus, crude o-methoxybenzoylosmocene was obtained in about 45% yield by treatment of osmocene with excess o-methoxybenzoyl chloride and aluminum chloride in refluxing methylene chloride for one week under anhydrous conditions. Even with the lengthy reaction time, recovery of osmocene was 47% and of the acid chloride (as the acid) 56%. Perhaps

an unacylable complex, $(C_5H_5)_2Os \cdot HA lCl_4$, formed as in the analogous cases of certain Friedel-Crafts reactions on ferrocene (29). In an initial run, workup after 20 hrs. reaction time indicated that 86% of the osmocene remained unreacted and the *o*-methoxybenzoyl chloride had self-condensed. Thus, little, if any, *o*-methoxybenzoic acid was obtained upon hydrolysis and the acid isolated contained new carbonyl groups. In a second run, solvent and acid chloride were freshly purified and an effort made to assure that the $AlCl_3$ employed was completely anhydrous; recovery of osmocene after 16 hrs. was 73%, and *o*-methoxybenzoic acid was obtained after hydrolysis in 71% yield. A third run with a different order of addition gave essentially the same results. Incidentally, it was noted that recovered osmocene did not show a band in the infrared at 11.4μ until the sample was sublimed. The presence of the band, then, was dependent upon crystal structure.



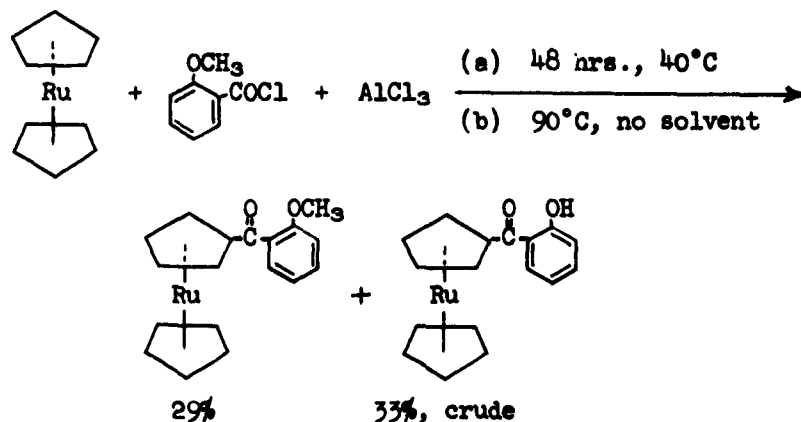
During an attempted preparation of *o*-methoxybenzoyl osmocene by the procedure that had given a 45% yield, the reaction mixture went to dryness over a weekend, and the product isolated proved to be *o*-hydroxybenzoyl osmocene (25%), along with some unreacted osmocene (31%). This formation of the *o*-hydroxy compound from osmocene was analogous to the known formation of *o*-hydroxybenzophenone from benzene, although a solvent was always present in the latter case (30). Results of an attempt to prepare *o*-hydroxybenzoyl ferrocene from ferrocene by the one-isolation process were not promising (1). In an effort to prepare the osmocene derivative under more controlled conditions, osmocene was treated with the acid chloride and aluminum chloride as before, the solvent removed in a 90° bath, and the residue heated in the bath 5.5 hrs. All the intermediate *o*-methoxybenzoyl osmocene was cleaved to the hydroxy compound by this procedure, but the amount of intermediate must have been lower than

before, inasmuch as the recovery of osmocene was 65%; the yield of crude *o*-hydroxybenzoylosmocene was nevertheless 24%. The first step appeared to be unusually sensitive to impurities.



F. Ruthenocene Derivatives

Unlike osmocene, ruthenocene is attacked at both cyclopentadienyl rings when treated with an excess of an aroyl chloride and aluminum chloride (22). The procedure used for preparation of *o*-hydroxybenzoylosmocene from a large excess of reagents was therefore not employed with ruthenocene, but instead a ratio of 1:1:1 ruthenocene-*o*-methoxybenzoyl chloride-aluminum chloride was used. The reaction yielded 29% *o*-methoxybenzoylruthenocene as well as 33% crude *o*-hydroxybenzoylruthenocene. This incomplete cleavage of the intermediate methoxy compound was also encountered with *o*-methoxybenzoylferrocene, with which two equivalents of aluminum chloride were required for complete cleavage (1).



The ruthenocene for this reaction was prepared from cyclopentadienyl-sodium and ruthenium trichloride in 12-21% yields by a known procedure (24). The reaction of bis(cyclopentadienyl)-magnesium with ruthenium trichloride in refluxing toluene was also examined in a single run, and 6% ruthenocene was isolated. The latter method has been useful for preparation of cyclopentadienyl metal compounds from soluble metal chlorides (31).

G. Spectra and Physical Properties of Candidate Compounds.

Absorption spectra in the 2100-5000 Å range for the o-hydroxybenzoyl derivatives of ruthenocene and osmocene are shown in Figures 2 and 3, respectively, and data from which the spectra were plotted are given in Tables III and IV. As anticipated, absorption in the visible region was significantly less for the ruthenocene and osmocene compounds than that of the ferrocene analog (1). The spectra for ferrocene, ruthenocene, and osmocene are compared in Figure 4, and the spectrum for o-methoxybenzoylruthenocene is given in Figure 5.

Infrared spectra of analytically pure cyclopentadiene and metallocene derivatives prepared as described in this report and in Parts I and II of this report are shown in Figures 6 to 54.

Certain physical properties of ruthenocene and three derivatives of ruthenocene and osmocene are presented in Table IV.

TABLE I
SUBSTITUTED CYCLOPENTADIENES, C₅H₅ R

No.	R	Formula	$\lambda_{\text{max}}, \text{\AA}$ (log ϵ) ^a	Infrared ^b Absorption	n_D^{25}	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
1	CH ₂ CH ₂ COOCH ₃	C ₉ H ₁₂ O ₂	2490 (3.43)	11.10, 11.25	1.4719	71.02	71.19	7.95	7.90
2	CH ₂ CH ₂ COOCH ₃ ^c	C ₁₃ H ₁₈ O ₄	2460 (2.63)	11.0-11.2	1.4779	65.53	55.59	7.61	7.60
3	CH ₂ CN	C ₇ H ₇ N	2440 (3.55)	11.20	1.4851	79.95	79.99	6.71 13.34 ^d	6.78 13.50 ^d
4	CH ₂ CH(OCH ₂ CH ₃) ₂	C ₁₁ H ₁₈ O ₂	2480 (3.59)	11.18, 11.26	1.4548	72.49	72.23	9.95	9.84
5	CH ₂ CH ₂ OH	C ₇ H ₁₀ O	2460 (3.10)	11.19, 11.25	1.4917	76.32	76.46	9.15	9.24

^a In cyclohexane for compounds 1, 2, and 4, and in ethanol for compounds 3 and 5.

^b In the 11 to 11.3 μ region.

^c R in C₅H₄R₂, a disubstituted cyclopentadiene.

^d Nitrogen, %

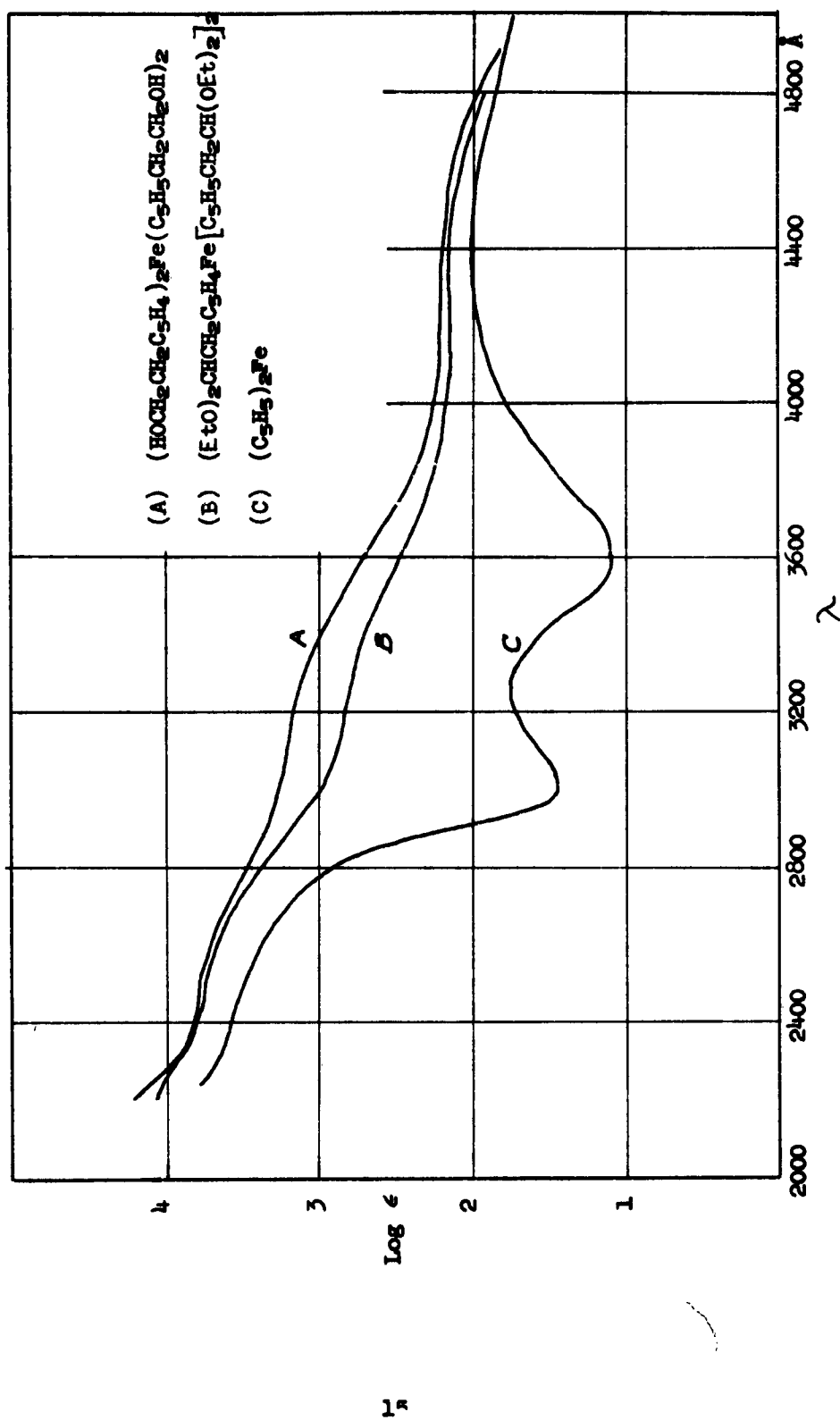


Figure 1. Absorption Spectra of (A) Bis(β -hydroxyethylcyclopentadienyl)-iron Bis(β -hydroxyethylcyclopentadiene), (B) β,β -Diethoxyethylcyclopentadienyl-iron Bis(β,β -diethoxyethyl)-cyclopentadiene, and (C) Ferrocene in Ethanol.

III. EXPERIMENTAL

Melting points were taken in sealed tubes under nitrogen and are uncorrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville 21, Tenn. All distillations of cyclopentadienyl or ferrocenyl compounds were conducted under nitrogen, and cyclopentadienyl compounds were stored below 0°C.

A. Ferrocenes from Cyclopentadiene

β -Carbomethoxyethylcyclopentadiene and Bis(β -carbomethoxyethyl)-cyclopentadiene. Under a nitrogen stream, 11.5 g. (0.5 mole) of sodium was added to 500 ml. of tetrahydrofuran* and followed by 50 ml. of cyclopentadiene. After the mixture was stirred 45 min. at room temperature and refluxed 2 hrs. without nitrogen flow, an additional 6 ml. of cyclopentadiene was added through the condenser and the mixture refluxed until the sodium was gone (30 min.). The colorless solution of cyclopentadienylsodium (24) was cooled in a -70°C bath under a nitrogen stream, and 83.5 g. (0.5 mole) of methyl 3-bromopropionate was added in one portion; the temperature rose to about 25°C. After the mixture was stirred 10 min. without the bath, 150 ml. of petroleum ether (30-60°C) was added, the mixture was poured into water and the aqueous layer was extracted with ether. The organic layers were combined, dried with magnesium sulfate, and solvent removed in vacuo at or below room temperature. Distillation of the residue under nitrogen through a short Vigreux column gave 34.1 g. (45%) of β -carbomethoxyethylcyclopentadiene, b.p. 46-48.5°C/0.2-0.6 mm., 15.7 g. of material, b.p. 104-110°C/0.3 mm., and left essentially no residue. Redistillation of the first fraction furnished compound 1, Table I, b.p. 51-51.5°C/0.7 mm. Redistillation of the second fraction gave 4.2 g. (6%) of additional β -carbomethoxyethylcyclopentadiene, b.p. 51-58°C/0.7 mm., and 8.91 g. (15%, based on the halide) of bis(β -carbomethoxyethyl)-cyclopentadiene (compound 2, Table I), b.p. 112-122°C/0.7 mm.

(Cyanomethyl)-cyclopentadiene. In the manner of the preceding experiment, 37.8 (0.5 mole) of chloroacetonitrile was added to cyclopentadienylsodium in tetrahydrofuran at -50°C, the mixture was maintained at 5-12°C for 10 min., after an exotherm near -20°C, and 50 ml. of petroleum ether was added. The mixture was then worked up as above, the organic material distilled**, and the distillate collected in a receiver in a -70°C bath to give 21.2 g. (40%) of (cyanomethyl)-cyclopentadiene, b.p. mainly 35-38°C/0.8 mm. (later fractions as low as 28°C). The residue (16 g.) was a soluble tar. Material trapped at -70°C beyond the receiver was redistilled to give an additional 1.4 g. (3%)

* Freshly distilled into the reaction flask from lithium aluminum hydride under nitrogen.

** The distillation was in part a slow depolymerization with the pot temperature finally at 210°C.

of the nitrile, b.p. 33°C/0.6 mm. Over half the product remained unpolymerized after 2 days at -70°C. Redistillation gave 16.6 g. (32%) of compound 3, Table I, b.p. 32-34°C/0.6 mm. (when the rate was 5 drops/min.).

In an initial run, in which distillation was too rapid for complete depolymerization, a sharp fraction, b.p. 142°C/0.13 mm., was obtained and assumed to be dimerized (cyanomethyl)-cyclopentadiene. Infrared bands at 11 to 11.3 μ were medium - weak.

Benzylcyclopentadiene. (1) From cyclopentadienylsodium. The method used for preparation of β -carbomethoxyethylcyclopentadiene was applied to benzyl chloride, except that the chloride was added at ice-bath temperature and the mixture refluxed for 15 hrs.; a vigorous exotherm occurred shortly after heating was begun. Distillation (partly a depolymerization) gave 1% benzyl chloride and 46% benzylcyclopentadiene, b.p. initially 130-137°C/13 mm. (later as low as 89°C/13 mm.) (lit. (3) b.p. 115-125°C/13 mm.). The infrared spectrum showed bands at 11.19 and 11.25 μ .

(2) From cyclopentadienyllithium. Cyclopentadienyllithium was prepared from 13.2 g. (0.2 mole) of cyclopentadiene in 100 ml. of tetrahydrofuran by addition of 85 ml. (0.137 mole) of 15% butyllithium in hexane below 17° during a 20-min. period. After the mixture was stirred 2 hrs. in an ice bath, 25.3 g. (0.2 mole) of benzyl chloride was added, the mixture was refluxed overnight, and water added. The organic layer was dried, taken to low volume, and distilled to give 10.0 g. (47%) of benzylcyclopentadiene, b.p. 97-127°C/5-11 mm.

β,β -Diethoxyethylcyclopentadiene. Compound $C_{12}H_{20}O_3$. In the manner described for preparation of benzylcyclopentadiene, cyclopentadienylsodium from 0.164 mole of sodium was treated with 0.164 mole of chloroacetaldehyde diethyl acetal to give 8.05 g. (27%) of β,β -diethoxyethylcyclopentadiene, b.p. 35-37°C/0.15-0.18 mm., and 11.1 g. of liquid, b.p. 80-135°C/0.09-0.18 mm. The second fraction was redistilled to give 0.93 g. (3%) of additional product, b.p. 30-33°C/0.15 mm. Redistillation of the combined acetal fractions furnished 7.2 g. (24%) of compound 4, Table I, b.p. 34°C/0.16 mm. A test for chlorine was negative.

Continued distillation of the second fraction furnished 7.3 g. of liquid, b.p. 88-114°C/0.5 mm., which might be expected to be either dimeric β,β -diethoxyethylcyclopentadiene or bis (β,β -diethoxyethyl)-cyclopentadiene. However, strong absorption in the ultraviolet at λ_{max} 2480 Å (log ϵ 3.31) (cyclohexane) eliminated the former and elemental analyses the latter. Inasmuch as the analyses and spectral data were consistent with a bis(β,β -diethoxyethyl)-cyclopentadiene from which ethanol had split out, the product was assumed to be 5,1-(α -diethoxymethyl- β -ethoxytrimethylene)-cyclopentadiene (35% yield).

Anal. Calc'd. for $C_{17}H_{30}O_4$: C, 68.42; H, 10.13.
 $C_{15}H_{24}O_3$: C, 71.39; H, 9.59.
Found: C, 71.79; H, 9.90.

When the experiment was repeated on a 1.97-mole scale, the yield of cyclopentadienylacetaldehyde diethyl acetal, b.p. $43^\circ\text{C}/0.3\text{ mm.}$, n_D^{25} 1.4542, was 105 g. (29%) after two distillations. The yield of material b.p. $80^\circ\text{C}/0.13\text{ mm.}$ to $130^\circ\text{C}/0.3\text{ mm.}$ was 111 g. (45%), n_D^{25} 1.4709. In addition, 57 g. of liquid b.p. $130\text{--}143^\circ\text{C}/0.3\text{ mm.}$, n_D^{25} 1.4662, was obtained and analyzed; it showed absorption typical of a cyclopentadiene at λ_{max} 2460 Å ($\log \epsilon$ 3.6) (ethanol).

Anal. Found: C, 71.92; H, 10.55.

β -Hydroxyethylcyclopentadiene. To 132 g. (2 mole) of cyclopentadiene in 1000 ml. of dry tetrahydrofuran in an ice bath was added 840 ml. (1.35 mole) of 15% butyllithium in hexane below 15° under nitrogen, and the mixture stirred 1 hr. Ethylene oxide (150 ml.; 3 mole) was added in one portion under a -70° condenser and the ice bath was replaced by a hot water bath until the temperature reached 50°C . The temperature continued to rise, and near 40°C it rose rapidly. Quick application of an ice bath lowered the temperature from 50°C to about 40° ; the mixture became lumpy. After an additional 1 hr. at $36\text{--}43^\circ\text{C}$ without external heating, the mixture was treated with 1 liter of water under nitrogen, the aqueous phase extracted with ether, and the combined organic layers dried and evaporated in vacuo to low volume. Distillation gave a 13.3-g. fraction, b.p. $25\text{--}44^\circ\text{C}/0.3\text{--}0.6\text{ mm.}$, which upon redistillation furnished 11.2 g. (5%) of β -hydroxyethylcyclopentadiene (compound 5, Table I), b.p. $33\text{--}34^\circ\text{C}/0.3\text{ mm.}$

Continued distillation yielded 41.6 g. (13.5%) of crude bis(β -hydroxyethyl)-cyclopentadiene (2), b.p. $118\text{--}150^\circ\text{C}/0.4\text{--}0.5\text{ mm.}$, which upon redistillation gave 21.5 g. of liquid, b.p. $115\text{--}137^\circ\text{C}/0.3\text{ mm.}$ Acidification of the original aqueous layer gave 40.9 g. of glassy solid, which was now insoluble in base; the infrared spectrum resembled that of bis(β -hydroxyethyl)-cyclopentadiene but with less hydroxyl absorption.

In a second run, 1240 ml. (2 mole) of butyllithium was employed, with all other quantities unchanged, but the amount of β -hydroxyethylcyclopentadiene isolated was negligible. There was obtained 1.1 g. of material, b.p. $45\text{--}62^\circ\text{C}/0.6\text{ mm.}$, 64.6 g., b.p. $62\text{--}165^\circ\text{C}/0.6\text{ mm.}$, and 12 g. of residue.

6-Carbethoxy-3,4-dihydrofulvene (Crude). Ethyl chloroacetate was substituted for methyl 3-bromopropionate in the above procedure for β -carbomethoxyethylcyclopentadiene and the reaction mixture stirred overnight at room temperature; an exotherm occurred near -10°C . After two distillations, 21.2 g. (28%) of 6-carbethoxy-3,4-dihydrofulvene was obtained, b.p. $45\text{--}47^\circ\text{C}/0.3\text{--}0.4\text{ mm.}$, n_D^{25} 1.5049, λ_{max} 2680 Å, ($\log \epsilon$ 4.22) (ethanol). Absorption in the infrared at $5.85\text{ }\mu$ (medium) suggested that the product was contaminated with a singly conjugated ester. The infrared spectrum also showed strong bands at 5.95 , 6.24 , 8.36 , and $8.93\text{ }\mu$.

Anal. Calc'd. for $C_8H_{12}O_2$: C, 71.02; H, 7.95.
Found: C, 70.94; H, 7.85.

Redistillation of a fraction, b.p. 85-180°C/1.3 mm., furnished 0.5 g. (0.7%) of additional diene, b.p. 40-45°C/0.3 mm., and 7.2 g. (12%) of liquid, b.p. 118-121°C/0.2 mm., n_D^{25} 1.4944, λ_{max} 2680 Å (log ϵ 4.17) (ethanol). The infrared spectrum showed strong bands at 5.83, 5.94, 6.23, and 7.8-8.9 μ , and a medium-weak band at 11.2 μ . The spectral data and analyses indicated that the liquid was carbethoxymethyl-6-carbethoxy-3,4-dihydrofulvene.

Anal. Calc'd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61.
Found: C, 65.70; H 7.63.

Reaction of Cyclopentadienylsodium with Ethylene Dichloride. Crude Vinylcyclopentadiene. In the manner described above for preparation of benzylcyclopentadiene, cyclopentadienylsodium was prepared from 0.5 mole of sodium and treated with 99 g. (1 mole) of ethylene dichloride. Distillation gave 7.7 g., b.p. 55-65°C/55-65 mm., 11.0 g., b.p. 70-88°C/25-45 mm., and 2.5 g. of residue. Redistillation of the first fraction through a short Vigreux gave 5.0 g. (22%) of crude vinylcyclopentadiene, b.p. 49-54°C/80 mm., n_D^{25} 1.5014, λ_{max} 2550 Å (log ϵ 4.00) (ethanol). The given calculated analyses are for vinylcyclopentadiene containing 8.4% ethylene dichloride; the chlorine content was too low for that of a pure chloro-compound of this volatility.

Anal. Calc'd.: C, 85.53; H, 8.35; Cl, 6.02.
Found: C, 86.08; H, 7.86; Cl, 6.36.

Redistillation of the second fraction gave 7.3 g. (16% or 32%) of a hydrocarbon, b.p. 70-76°C/25 mm., n_D^{25} 1.5093, λ_{max} 2600 Å (log ϵ 0.8, ca.). The ultraviolet spectrum showed that the compound was not a cyclopentadiene (absorption very weak) while the infrared spectrum indicated unsaturation (weak bands at 6.18, 6.27, and 6.43 μ).

Anal. Calc'd. for $C_{14}H_{18}$: C, 90.26; H, 9.74.
Found: C, 90.49; H, 9.57.

Reaction of Cyclopentadienyllithium with Epichlorohydrin. To 13.2 g. (0.2 mole) of cyclopentadiene in 100 ml. of tetrahydrofuran in an ice bath under nitrogen was added 84 ml. (0.135 mole) of 15.3% butyllithium in hexane during a 40-min. period. After the mixture was stirred 1 hr. in the bath, 18.5 g. (0.2 mole) of epichlorohydrin was added, and the bath removed; 15 min. later a mild exotherm was noted. The mixture was stirred 1 hr. at room temperature, stored overnight at 0°C, and treated dropwise with 50 ml. of cold water. The aqueous phase was extracted with ether, the combined organic layers dried and taken to low volume below room temperature. Distillation of the residue (10 ml.) gave 2.90 g. of liquid, b.p. 40-42°C/0.07-0.10 mm.; the infrared spectrum showed a strong hydroxyl band.

Anal. Calc'd. for $C_{20}H_{14}ClO$: C, 60.57; H, 6.99; Cl, 22.35.
Found: C, 70.59; H, 8.40; Cl, 9.54.

Continued distillation up to a pot temperature of $250^{\circ}C$ gave 1.3 g. of distillate.

1,1'-Dibenzylferrocene. (1) Via Methyllithium. Methyl iodide (56.8 g.; 0.4 mole) in 100 ml. of dry ether was added to 5.74 g. (0.826 mole) of lithium slices in 350 ml. of dry ether under nitrogen during a 1.5-hr. period, the mixture stirred 30 min., and refluxed 30 min. To 12.1 g. (0.0775 mole) of crude benzylcyclopentadiene in 100 ml. of dry tetrahydrofuran was added dropwise 106 ml. of the methyllithium solution during a 30-min. period; further addition of 5 ml. of solution did not cause gas evolution. Ferrous chloride (6.9 g.; 0.054 mole) was added, the mixture was stirred 48 hrs. at room temperature, and treated with 200 ml. of petroleum ether. Water was added and the organic phase was dried and taken to dryness. Crystallization of the residue from hexene gave 10.2 g. (72%) of crude product, m.p. $96-100^{\circ}C$, which, after recrystallization, chromatography on alumina, and recrystallization gave 6.43 g. (45%) of 1,1'-dibenzylferrocene, m.p. $102-103^{\circ}C$ (lit. m.p. $101.5-102.5^{\circ}C$ (32); $105-106^{\circ}C$ (33)).

(2) Via Sodium Dispersion (Unsuccessful). A mixture of 10.04 g. (0.0641 mole) of benzylcyclopentadiene, 75 ml. of dry 1,2-dimethoxyethane, and 2.76 g. (0.06 mole) of 50% sodium dispersion in mineral oil was stirred 1 hr. and heated almost to reflux for 30 min. Very little sodium remained. The mixture was cooled in an ice bath, treated with 3.80 g. (0.03 mole) of ferrous chloride, and refluxed overnight. Petroleum ether was added, the mixture poured into water, filtered, and the organic layer taken to dryness. The residual 10.72 g. of liquid was chromatographed on alumina, but only 2.98 g. of colored material was obtained and this in two different fractions. The infrared spectrum of the main fraction showed that it contained considerable material other than dibenzylferrocene.

1,1'-Bis(β,β -diethoxyethyl)-ferrocene. Compound $C_{30}H_{22}FeO_2$. (1) Run 1. Isopropylmagnesium chloride solution was prepared by dropwise addition of 3.2 ml. of isopropylmagnesium chloride to 0.91 g. (0.0374 mole) of magnesium in 9 ml. of dry ether, after the reaction had been initiated by a drop of ethyl bromide and 1.0 ml. of isopropyl chloride. The solution was added in 5 min. to 6.16 g. (0.0338 mole) of β,β -diethoxyethylcyclopentadiene in 40 ml. of dry tetrahydrofuran at -10° to $-7^{\circ}C$ under nitrogen, the mixture was stirred 25 min. at -10° to $-14^{\circ}C$, and 2.14 g. (0.0169 mole) of ferrous chloride was added in one portion. The cooling bath was removed but applied again after about 10 min. to prevent loss by frothing. After the mixture was stirred overnight without the bath, it was added to water along with 50 ml. of petroleum ether. The aqueous layer was extracted with chloroform, filtered, and the combined organic layers dried. Removal of solvent and rapid distillation of the residue (6.4 g.) gave 1.50 g. (24%) of recovered acetal, b.p.

32-37°C/0.12 mm., 1.18 g. of an intermediate fraction, and 2.75 g. (39%) of 1,1'-bis(β,β -diethoxyethyl)ferrocene, b.p. 156°C/0.12 to 162°C/0.20 mm., n_D^{25} 1.5096.

Anal. Calc'd. for $C_{22}H_{34}FeO_4$: C, 63.16; H, 8.19; Fe, 13.35.
Found: C, 63.36; H, 8.35; Fe, 13.43.

In order to establish the product as an acetal, 0.5 g. of the distilled product was heated in a mixture of 5 ml. of dioxane and 3 ml. of 2% hydrochloric acid for 3 min., cooled, and the mixture extracted with ether. The extract was dried and taken to dryness. The infrared spectrum of the residual thick oil (0.36 g.) showed a strong carbonyl band at 6μ and medium carbonyl bands at 5.8 and 6.1μ , as well as a medium hydroxyl band at 2.98μ .

(2) Run 2. The procedure used in Run 1 was repeated except that the mixture, after addition of isopropylmagnesium chloride, was stirred 2 hrs. at -10 to -20°C instead of 25 min.; a gelatinous precipitate was present. After ferrous chloride was added, the mixture was stirred two days. Distillation gave 3.73 g. (61%) of starting acetal (infrared comparison), b.p. 39-42°C/0.3 mm., and left 0.63 g. of orange brown residue.

(3) Run 3. The procedure of Run 1 was employed with 0.5 mole of the acetal and 0.555 mole of magnesium. Distillation of an aliquot gave 6.10 g. (27%) of starting acetal, b.p. 28-34°C/0.03-0.14 mm. Slow continued distillation resulted in decomposition, and no ferrocenes were isolated. A second aliquot was chromatographed on Florisil in petroleum ether by elution with petroleum ether, 1:1-petroleum ether-benzene, benzene, and 2:1 benzene-ether. Material eluted with the last eluant was kept in a bath at 85°C/0.5 mm. to remove starting material; the infrared spectrum of the residue was the same as that of the desired ferrocene (13.5% yield). A third aliquot was filtered through a column of Florisil in chloroform and eluted with chloroform and with ether. Material eluted with chloroform was distilled at an average rate to give 9.78 g. (24%) of starting acetal and 5.96 g. (13%) of 1,1'-bis(β,β -diethoxyethyl)-ferrocene, b.p. 152°C/0.45 mm. to 172°C/1.0 mm.; the residue weighed 6.92 g. Material eluted with ether was removed as a small sharp band (0.85 g.), elemental analyses on which agreed fairly well for a structure containing three β,β -diethoxyethylcyclopentadienyl groups per iron atom (2% yield).

Anal. Calc'd. for $C_{33}H_{52}FeO_6$: C, 65.99; H, 8.73; Fe, 9.30.
Found: C, 65.29; H, 8.77; Fe, 9.02.

Crude Bis[5,1-(α -diethoxymethyl- β -ethoxytrimethylene)-cyclopentadienyl]-iron. Compound $C_{20}H_{24}FeO_3$. Compound $C_{15}H_{24}O_3$ described above (6.2 g.) was treated with isopropylmagnesium chloride as in the preparation of 1,1'-bis(β,β -diethoxyethyl)-ferrocene, Run 1, except that the mixture was stirred 3 hrs. in an ice-bath prior to addition of ferrous chloride (1.32 g.). The mixture was stirred overnight and worked up as usual to give 3.83 g. (62%) of

starting material, b.p. 82-105°C/0.07-0.09 mm. Chromatography of the distillation residue (1.87 g.) on Florisil in petroleum ether by elution with 1:1 benzene-ether gave 1.39 g. of orange liquid, which was then micro-distilled twice at 150-210°C/0.025 mm.; n_D^{25} 1.4977. Elemental analysis showed that this ferrocene was impure.

Anal. Calc'd. for $C_{30}H_{40}FeO_2$: C, 64.51; H, 8.30; Fe, 10.00.
Found: C, 64.36; H, 8.83; Fe, 8.42.

Subsequent elution with acetone gave 0.20 g. (3%) of red oil, elemental analyses for which agreed with a structure containing four of the starting cyclopentadienyl groups per iron atom.

Anal. Calc'd. for $C_{60}H_{84}FeO_{12}$: C, 67.78; H, 8.91; Fe, 5.25.
Found: C, 67.17; H, 9.06; Fe, 5.29.

1,1'-Bis(β -hydroxyethyl)-ferrocene. Compound $C_{26}H_{36}FeO_4$. A solution of 9.75 g. (0.0885 mole) of β -hydroxyethylcyclopentadiene in 75 ml. of dry tetrahydrofuran under nitrogen in an ice bath was treated with 77 ml. (0.124 mole) of 15% butyllithium in hexane during a 30-min. period. After 1.5 hrs., 5.60 g. (0.0443 mole) of ferrous chloride was added to the slightly opaque solution and the mixture stirred overnight without the bath. It was then added to a solution of 10 ml. of concentrated hydrochloric acid in 100 ml. of water, the aqueous layer and oil extracted with chloroform, and the combined organic layers dried and taken to dryness. The residue was distilled to remove unreacted β -hydroxyethylcyclopentadiene (1.35 g. (14%), b.p. 25-32°C/0.2-0.35 mm.), the distillation residue (6.52 g.) was dissolved in 16 ml. of chloroform, and one-fourth of the solution was chromatographed on Florisil in benzene. Elution with benzene and benzene-ether was unfruitful, but subsequent elution with ether slowly removed 0.89 g. of colored material, which after two careful crystallizations from ether (finally at -70°C) gave 0.59 g. (19%) of 1,1'-bis(β -hydroxyethyl)-ferrocene, m.p. 43-45°C.

Anal. Calc'd. for $C_{14}H_{18}FeO_2$: C, 61.34; H, 6.62; Fe, 20.37.
Found: C, 61.31; H, 6.76; Fe, 20.52.

Subsequent elution with acetone removed 0.45 g. of liquid, which was extracted with dry ether, the extract taken to dryness, and the residue extracted with 20 ml. of dry ether. Removal of solvent from the extract left 0.35 g. (13%) of amber oil, elemental analyses on which agreed fairly well for a compound containing four β -hydroxyethylcyclopentadienyl groups per iron atom.

Anal. Calc'd. for $C_{26}H_{36}FeO_4$: C, 68.01; H, 7.75; Fe, 11.30.
Found: C, 67.48; H, 7.78; Fe, 10.83.
11.15

Hydrogenation of 0.23 g. of the amber oil in 50 ml. of ethanol at 50 lbs./sq. in. hydrogen with 0.03 g. of palladium on charcoal as catalyst did not alter the ultraviolet spectrum of the solution.

1,1',x,x'-Tetrakis(β -hydroxyethyl)-ferrocene (Unsuccessful). Methylolithium in ether (see "1,1'-Dibenzylferrocene" above) was added to 3.53 g. (0.0229 mole) of crude bis(β -hydroxyethyl)cyclopentadiene in 90 ml. of dry tetrahydrofuran until no significant gas evolution occurred on further addition. The addition time was approximately 3 hrs., with 0.5 to 1 hr. intervals between the last two 10-ml. additions. The volume of the mixture was reduced to about 125 ml. by distillation, 1.46 g. (0.0115 mole) of ferrous chloride was added, and the mixture was stirred for 5 days. Water was added and the mixture filtered; the solid was insoluble in chloroform or ether. Extraction of the homogeneous filtrate with ether or chloroform did not yield a colored extract. Removal of solvent from the aqueous solution and decantation left non-combustible solids. Addition of acetone to the decanted solution precipitated 1.13 g. of combustible solid. The filtrate was taken to dryness, but chromatography of the residue on Florisil was unfruitful.

1,1'-Bis(cyanomethyl)-ferrocene (Unsuccessful). (1) At -20°C . To 50 ml. of tetrahydrofuran in a -70° bath was added 4.67 g. (0.0444 mole) of (cyanomethyl)-cyclopentadiene under nitrogen and followed by 62 ml. (0.05 mole, ca.) of methylolithium solution in ether (see "1,1'-Dibenzylferrocene" above) during a 10-min. period; gas was evolved. Ferrous chloride (3.17 g.; 0.025 mole) was then added. After the mixture was kept at -20 to -30°C for 7.5 hrs., 100 ml. of water was added, the water layer was extracted with ether and with chloroform with filtration, and the combined extracts were dried and taken to dryness; 4.89 g. of residue remained. Chromatography on 100 g. of Florisil in 1:1 benzene-petroleum ether by elution with benzene and ether gave some starting nitrile (infrared comparison; it polymerized on standing). Elution with chloroform was unfruitful and acetone yielded 1.05 g. of tar. The tar was dissolved in 5 ml. of chloroform, filtered, and the filtrate treated with dry ether to precipitate 0.26 g. of a brown solid, which was analyzed; the filtrate was not highly colored. After three weeks at room temperature, the solid was no longer soluble in chloroform.

Anal. Calc'd. for $(\text{C}_7\text{H}_7\text{N})_2\text{Fe}$: C, 72.60; H, 6.09; N, 12.10; Fe, 0.00.
Found: C, 73.20; H, 5.66; N, 11.30; Fe, 0.42.
0.44

(2) At 25° . Isopropylmagnesium chloride solution (prepared from 0.11 mole of magnesium in ether) was added to 10.5 g. (0.1 mole) of (cyanomethyl)-cyclopentadiene in 100 ml. of dry tetrahydrofuran below 0° under nitrogen, the mixture stirred at -10 to -15° for 2 hrs., and 0.05 mole of ferrous chloride added. When the mixture was stirred at room temperature overnight, a lump of gummy solid formed. Petroleum ether (50 ml.) and 80 ml. of water were added. From the organic layer, 1.98 g. of material was obtained, and

extraction of the aqueous layer and insoluble solids with chloroform gave 4.28 g. of additional material. Washing the combined product with ether left 5.42 g. of glassy powder, only about half of which was now soluble in chloroform. Filtration of the chloroform-soluble part through alumina in chloroform gave 1.5 g. of colored oil, which was still soluble in chloroform after overnight exposure to air.

B. Urethanes from 1,1'-Ferrocene Diisocyanate.

Dimethyl 1,1'-Ferrocenedicarbamate. 1,1'-Ferrocene diisocyanate (0.5 g.) was dissolved in 13 ml. of methanol, filtered quickly with 4 ml. of methanol as wash, and the filtrate cooled after 1 hr., finally at -70° . Filtration and washing with cold methanol gave 0.48 g. (77%) of dimethyl 1,1'-ferrocenedicarbamate, m.p. $177-177.5^{\circ}\text{C}$.

Anal. Calc'd. for $\text{C}_{14}\text{H}_{12}\text{FeN}_2\text{O}_4$: C, 50.62; H, 4.86; Fe, 16.81; N, 8.44.
Found: C, 50.75; H, 4.70; Fe, 17.00; N, 8.48.

Diethyl 1,1'-Ferrocenedicarbamate. Substitution of 15 ml. of ethanol for methanol in the preceding experiment yielded 0.48 g. (72%) of diethyl 1,1'-ferrocenedicarbamate, m.p. $119.5-120^{\circ}\text{C}$.

Anal. Calc'd. for $\text{C}_{16}\text{H}_{20}\text{FeN}_2\text{O}_4$: C, 53.35; H, 5.60; Fe, 15.50; N, 7.78.
Found: C, 53.49; H, 5.77; Fe, 15.30; N, 7.83.

Poly(1,1'-ferrocenedimethyl 1,1'-Ferrocenedicarbamate). (1) Tetrahydrofuran as solvent. To 0.50 g. (0.002 mole) of 1,1'-di(hydroxymethyl)-ferrocene (2) in 10 ml. of dry tetrahydrofuran was added 0.54 g. (0.002 mole) of 1,1'-ferrocene diisocyanate under nitrogen. The homogeneous mixture soon became warm. After it was allowed to stand overnight, the mixture was added dropwise to 25 ml. of anhydrous ether, filtered, and the solid washed with ether to give 0.82 g. (79%) of the polyurethane, m.p. $65-150^{\circ}\text{C}$, ca. It was soluble in tetrahydrofuran and chloroform, but insoluble in warm methyl ethyl ketone. The infrared spectrum showed no isocyanate band. The filtrate yielded additional solid polymer (11%).

Anal. Calc'd. for $(\text{C}_{24}\text{H}_{22}\text{Fe}_2\text{N}_2\text{O}_4)_n$: C, 56.06; H, 4.31; N, 5.45.
Found: C, 56.26; H, 4.52; N, 5.52.
56.30 4.48 5.33

In an initial run, a trace of dibutyltin dilaurate was added as catalyst and an attempt was made to chromatograph the product. When alumina in chloroform was used, no adsorption occurred, while with alumina in benzene, the polymer gummed out on the column and was not readily removed.

(2) Benzene as solvent. To 1.00 g. (0.00373 mole) of 1,1'-ferrocene diisocyanate dissolved in 10 ml. of dry benzene under nitrogen was added 0.92 g.

(0.00373 mole) of 1,1'-di(hydroxymethyl)-ferrocene and a trace of dibutyltin dilaurate. The heterogeneous mixture (the diol was only partly soluble) was stirred 2 hrs., during which time a precipitate formed. After the mixture was allowed to stand overnight, it was filtered and the solid washed with benzene. Shaking the solid (1.84 g.; 96%) 1 hr. in 18 ml. of dry tetrahydrofuran, filtering, and shaking 1 hr. with a second 18 ml. left 1.22 g. (64%) of polyurethane, m.p. 135->300°C, insoluble in chloroform and in tetrahydrofuran. The infrared spectrum differed from the above soluble polyurethane essentially only in the 7-8 μ and 13-14 μ regions.

Anal. Calc'd. for $(C_{24}H_{22}Fe_2N_2O_4)_n$: C, 56.06; H, 4.31; N, 5.45.
Found: C, 56.23; H, 4.57; N, 5.59.

Differential Thermal Analysis on Urethanes from 1,1'-Ferrocene Diisocyanate. (1) Dimethyl 1,1'-ferrocenedicarbamate in alumina. An endotherm occurred at 182-192°C (m.p. 177-177.5°C), and a second endotherm (decomposition) began near 245°C and proceeded to an exotherm near 285°C.

(2) Diethyl 1,1'-ferrocenedicarbamate. An endotherm occurred at 121-127°C (m.p. 119.5-120°C), and a second endotherm (decomposition) began at 255°C and proceeded to a large exotherm at 288°C.

(3) Soluble poly(1,1'-ferrocenedimethyl 1,1'-ferrocenedicarbamate) in alumina. A small endotherm occurred from 115-160°C, a weaker exotherm from 250-290°C, and a major exotherm at 315°C.

(4) Insoluble poly(1,1'-ferrocenedimethyl 1,1'-ferrocenedicarbamate) in alumina. An endotherm occurred from about 110°-240°C followed at 280°C by a broad exotherm.

Hydrolysis of 1,1'-Ferrocene Disocyanate. A solution of 0.2 g. (0.745 mmole) of 1,1'-ferrocene diisocyanate (2)* in 1 ml. of dry tetrahydrofuran was added to a mixture of 2 ml. of tetrahydrofuran and 1 ml. of water, with 1 ml. of tetrahydrofuran as wash. After the mixture was swirled 15 min., it was diluted with 5 ml. of water, allowed to stand 15 min., and filtered. The mixture was washed with ether to give 0.11 g. (61%) of insoluble solid, the infrared spectrum of which showed bands at 3.08 (w), 3.19 (w), 6.1 (m), and 6.3-6.5 μ (m), but none in the isocyanate region. Elemental analyses agreed fairly well with a poly(ferrocenyleneurea) structure. The material was insoluble in dimethylformamide and in dilute base, and it did not melt before decomposing.

Anal. Calc'd. for $C_{11}H_{10}FeN_2O$: C, 54.58; H, 4.16; N, 11.56.
Found: C, 54.25; H, 4.44; N, 10.82.

* After 10 mos. under nitrogen, only 1.55 g. of an original 9.3 g. of the diisocyanate was soluble in benzene. The remainder had polymerized.

C. Miscellaneous Reactions on Ferrocene.

Diferrocenylmethanol. A mixture of 9.3 g. (0.05 mole) of ferrocene and 29.6 g. (0.2 mole) of ethyl orthoformate in 65 ml. of dry ethylene dichloride was stirred under nitrogen in an ice bath, 13.3 g. (0.10 mole) of granular anhydrous aluminum chloride was added, and the ice bath was removed. About 15 mins. after the mild exotherm was over, 26.6 g. (0.2 mole) of aluminum chloride was added in five portions 5 mins. apart, the mixture stirred overnight, re-fluxed 1 hr., and poured onto ice. The organic layer and a chloroform extract of the water layer were combined, dried, and solvent removed. The residue, 9.48 g., was combined with chloroform-soluble material (1.14 g.) obtained by reduction of the aqueous layer with zinc dust. Chromatography of the material in chloroform on alumina in 1:1 petroleum ether-benzene by elution with petroleum ether-benzene, 1:1 benzene-ether, ether, 1:1 chloroform-ether, and chloroform gave three bands: ferrocene (55%), an intermediate fraction (1.43 g.), and a final fraction (2.69 g.). Crystallization of the final fraction from toluene gave 1.78 g. (18%) of diferrocenylmethanol, m.p. 173-175°C (slow dec.) (lit. (34) 20% yield, m.p. 175-180° (dec.)).

Reaction of Ferrocene with Aluminum Chloride and Chloroacetaldehyde Diethyl Acetal. To 9.3 g. (0.05 mole) of ferrocene in 65 ml. of ethylene dichloride at -20°C was added 13.3 g. (0.10 mole) of aluminum chloride in one portion. To the mixture was added dropwise 15.3 g. (0.1 mole) of chloroacetaldehyde diethyl acetal during an 80-min. period, the mixture stirred 30 mins., and warmed to -5°C. It was then added to ice, the aqueous layer extracted with chloroform, and the combined organic layers dried and taken to dryness. The residue (5.92 g.) was extracted with 120 ml. of petroleum ether in 20-ml. portions and each portion added to 180 g. of alumina and eluted with petroleum ether to give 1.75 g. (19%) ferrocene. Continued elution with the usual solvents removed distinct fractions (oils), the infrared spectra of which suggested the ferrocenes present were monosubstituted. Reduction of the aqueous layer with zinc dust, extraction with chloroform, and removal of solvent left moist solid, which when extracted with methanol left 3.04 g. (33%) of crude ferrocene. Removal of methanol and chromatography of the residue (2.73 g.) gave 4% ferrocene and 1.65 g. of solid, m.p. 14-21°C, which was probably a monosubstituted ferrocene containing ether linkages (infrared).

Reaction of Ferrocene with Aluminum Chloride and 2,2-Dimethoxypropane.
Run 1. Addition of 0.1 mole of powdered aluminum chloride in one portion to a mixture of 0.05 mole of ferrocene and 0.2 mole of 2,2-dimethoxypropane in 65 ml. of ethylene dichloride under nitrogen produced an immediate uncontrollable exotherm. The mixture was cooled, poured into ice water, and the organic layer dried and taken to dryness. Chromatography of the residue in benzene on alumina in petroleum ether by elution with petroleum ether and benzene gave 11.6 g. of material, from which was obtained 5.1 g. (55%) of ferrocene by washing with petroleum ether. Elution with ether gave 5.1 g. of oil.

Run 2. The reaction was also run by addition of the aluminum chloride in 2-g. portions 5 mins. apart at -30° to the dimethoxypropane, followed by addition of a ferrocene solution. After stirring overnight at room temperature, the mixture was hydrolyzed and worked up as before to give 73% ferrocene and a filtrate containing some ferrocene.

Run 3. 2,2-Dimethoxypropane (0.4 mole) in methylene chloride was added dropwise to a mixture of 0.1 mole of ferrocene and 0.2 mole of aluminum chloride in methylene chloride at -30° during a 40-min. period and the mixture hydrolyzed 1 hr. later. Chromatography on alumina gave 80% recovered ferrocene; distillation of liquid products was unfruitful.

Reactions of Lithiated Ferrocene. 1. With acetaldehyde. A solution of 9.3 g. (0.05 mole) of ferrocene in 150 ml. of tetrahydrofuran at -30°C was treated with 130 ml. (0.21 mole) of 15% butyllithium in hexane and the mixture allowed to come to room temperature overnight. It was then added slowly to 17.6 g. (0.40 mole) of acetaldehyde in 100 ml. of dry ether under nitrogen in an ice-bath, the mixture stirred 1.5 hrs., and treated with 200 ml. of water. Evaporation of the dried organic layer (and an extract) in vacuo left 13.5 g. of residue, which upon chromatography on Florisil gave 5.31 g. (57%) of crude ferrocene, 2.46 g. of material the infrared spectrum of which indicated mono-substituted ferrocene (and carbonyl and hydroxyl groups), and 3.23 g. of a carbonyl-containing mixture.

2. With epichlorohydrin. The preceding experiment was repeated with epichlorohydrin in place of acetaldehyde and the mixture stirred overnight before hydrolysis (no notable reaction occurred during hydrolysis). The residue (15.7 g.) was chromatographed on Florisil to give 83% crude ferrocene and a carbonyl-containing liquid.

3. With benzaldehyde. The preceding experiment was repeated with 0.21 mole of benzaldehyde in place of 0.4 mole of epichlorohydrin. Chromatography of part of the residue (28.4 g.) on Florisil gave 30% crude ferrocene and three liquid fractions each probably containing some butylphenylcarbinol. Part of the residue was also kept under vacuum at $100-125^{\circ}\text{C}$ in an effort to remove the butylphenylcarbinol and ferrocene, and the residue was chromatographed on alumina. The main fraction was a liquid.

Chloroacetylferrocene. The procedure of K. Schlogl (35) was employed on 168 g. of ferrocene to give 16% chloroacetylferrocene, m.p. $83-85^{\circ}\text{C}$ or 8%, m.p. $90-91^{\circ}\text{C}$ (lit. 12%; m.p. $92-93^{\circ}\text{C}$).

1-Ferrocenyl-2-chloroethanol (Unsuccessful). (1) In isopropyl alcohol. Chloroacetylferrocene (5.24 g.; 0.02 mole) and 0.80 g. (0.0216 mole) of sodium borohydride in 40 ml. of isopropyl alcohol was refluxed 1.5 hrs., taken to dryness in vacuo, and treated with water. The mixture was extracted with ether, the extract dried and taken to dryness. The residue (4.84 g.) was

dissolved in ether and chromatographed on 40 g. of Florisil in petroleum ether by elution with petroleum ether-ether (0 to 100%). Crystallization of the eluted material from ether at -70°C gave 1.99 g. of yellow solid, m.p. $56-66^{\circ}\text{C}$. Recrystallization did not alter the melting point. The infrared spectrum showed a strong broad hydroxyl band. The yield of solid material was not improved by a reaction time of 5 hrs.

(2) In 1,2-dimethoxyethane. A mixture of 1.31 g. (0.0050 mole) of chloroacetylferrocene and 0.20 g. (0.0053 mole) of sodium borohydride in 10 ml. of 1,2-dimethoxyethane was stirred and refluxed for 5 hrs. Solvent was removed, the residue treated with water, and extracted with ether. The extract was dried, solvent removed, and the residue (1.24 g.) chromatographed on Florisil. The fractions were oils, and the infrared spectrum of the major fraction (an alcohol) differed significantly from that of the above solid alcohol.

D. New Organociron Complexes (Unsuccessful).

Reaction of Butadiene, Ethylmagnesium Chloride, and Ferrous Chloride. Ethylmagnesium chloride solution was prepared by addition of ethyl chloride in portions to 2.68 g. (0.11 mole) of magnesium in 27 ml. of dry ether containing 3 drops of ethyl bromide until the magnesium was almost gone upon 1 hr. reflux. To 50 ml. of tetrahydrofuran in a -70° bath was added the ethylmagnesium chloride solution, 10 ml. (0.12 mole) of butadiene, and 6.34 g. (0.05 mole) of ferrous chloride. The mixture was stirred in an ice bath for several hours, added to dilute hydrochloric acid, and the organic layer dried. Removal of solvent left 2.22 g. of residue. It was extracted with petroleum ether (0.06 g. insoluble) and chromatographed on 60 g. of Florisil in petroleum ether by elution with petroleum ether, 1:1 petroleum ether-benzene (1.28 g. liquid, iron-free), benzene, and ether. The final fraction was a red oil (0.16 g.) that gave a weak test for iron; the infrared spectrum was not inconsistent with a ferrocene-like structure (bands near 6μ and 12.5μ), but there was also significant hydroxyl absorption. Because the yield was very low and the test for iron unconvincing, the material was not further investigated.

Reaction of Allylmagnesium Chloride and Ferrous Chloride. Allylmagnesium chloride was prepared by the method described by Kharasch and Reinmuth (36) from 15.3 g. (0.2 mole) of allyl chloride and 5.34 g. (0.22 mole) of magnesium in a total of 85 ml. of dry ether. To the mixture was slowly added 85 ml. of tetrahydrofuran, the mixture cooled in a -70° bath under nitrogen, and treated with 6.34 g. (0.05 mole) of ferrous chloride. The bath was removed. After 2 hrs. above 20°C , the mixture was treated dropwise with dilute hydrochloric acid (considerable gas evolution) and finally poured into more dilute acid. The organic layer was dried and taken to dryness to give 2.38 g. of red oil. The oil was dissolved in petroleum ether and chromatographed on alumina. The main fraction (1.0 g.) was a pale yellow liquid, the infrared spectrum of which did not suggest the presence of an aromatic system (absence of significant absorption beyond 11.5μ). A sharp colored fraction (0.26 g.) proved to be silicone

oil with a colored contaminant. A second colored fraction (0.22 g.), removed with 2:1 ether-methanol, was not investigated because of its highly polar nature.

Reaction of Butadiene, 4-Methoxybutylmagnesium Chloride, and Ferrous Chloride. Treatment of 1,4-dichlorobutane with sodium methoxide by the method of R. C. Elderfield, et al. (37), gave 4-methoxybutyl chloride, b.p. 141-144.5°C, n_D^{20} 1.4226. To 2.68 g. (0.11 mole) of magnesium in 40 ml. of ether was added 3 drops of ethyl bromide and one-fourth of a 12.3 g. (0.1 mole) portion of 4-methoxybutyl chloride. After the reaction had begun, the remainder of the halide was added during a 30-min. period and the mixture refluxed overnight. The mixture was added to 50 ml. of tetrahydrofuran in a -70° bath and followed by 10 ml. (0.12 mole) of butadiene and 6.34 g. (0.05 mole) of ferrous chloride. After it was stirred in an ice bath several hours, the mixture was poured into dilute hydrochloric acid with the aid of a chloroform wash, the organic layer dried, and taken to dryness. Chromatography of the residue (5.9 g., fluid) gave 2.92 g. of liquid identical (infrared) with a material obtained from the above reaction of butadiene, ethylmagnesium chloride and ferrous chloride. Tests for iron on two colored fractions totaling 1.08 g. were very weak.

Reaction of Cyclopentadiene, Cyclopentadienyllithium, and Ferrous Chloride. To 49 ml. (0.6 mole) of cyclopentadiene in 230 ml. of dry tetrahydrofuran under nitrogen in an ice bath was added 124 ml. (0.2 mole) of 15% butyllithium in hexane during a 30-min. period. After the mixture was stirred for 30 min., 12.7 g. (0.1 mole) of ferrous chloride was added, and the mixture stirred in the bath for 3.5 hrs. It was poured into dilute hydrochloric acid, the aqueous layer extracted with ether, and the combined organic layers dried. Removal of solvent left 12.4 g. of solid. An additional 1.2 g. of solid was obtained by treating the aqueous layer with zinc dust. The solids were combined and extracted with 50 ml. of cold petroleum ether to give 11.83 g. of solid, which on sublimation yielded 60% ferrocene, m.p. 174.5-176°C, and left 0.25 g. of residue. The residue gave a weak test for iron and showed no significant absorption in the infrared beyond 7.5 μ . The petroleum ether extract yielded 0.63 g. (3%) of additional ferrocene, m.p. 172-174°C, and, upon complete evaporation, 0.85 g. of an orange solid containing a small amount of oil.

E. Osmocene Derivatives

Osmium Tetrachloride. The method of Ruff and Bornemann (26) was scaled up as follows. A 3-ft. length of 1-in. dia. Vycor tubing with ball joints at both ends was heated to 675-700°C in two 13-in. furnaces arranged in tandem, one of which was cold. After the tube was flushed with nitrogen, 11.9 g. of osmium sponge (10 mesh, from J. Bishop and Co. Platinum Works, Malvern, Pa.) was added in a porcelain boat, the tube flushed with nitrogen, and the exit end plugged lightly with glass wool in a 7-mm. constriction. Chlorine that was free of impurities detectable by infrared analysis was passed through H_2SO_4 and introduced into the tube at an entrance rate of about 3 to 4 bubbles per second. After chlorination for 65 hrs., the tube was allowed to cool under a nitrogen stream and the boat removed. The entrance end was then stoppered,

the osmium tetrachloride that had collected immediately beyond the hot zone was allowed to fall to the entrance end under nitrogen by scraping with a long rod, and the product was then dropped into a vessel filled with nitrogen by removal of the entrance plug. The yield of osmium tetrachloride was 15.1 g. or 85% based on consumed osmium (10.2 g.) (lit. (26) yield 50-65%). The product did not absorb in the infrared.

Anal. Calc'd. for OsCl_4 : Cl, 42.72; Os, 57.28.
Found: Cl, 42.67; Os, 56.87.

In four other runs, yields of 84%, 89%, 76%, and 84% were obtained.

Diosmium Oxide Octachloride.* The preceding procedure was applied to 8.00 g. of osmium with air bleeding into the chlorine stream at an air to chlorine bubble-ratio of about 1 to 15. A red-brown liquid formed and slowly crystallized well beyond the point of deposition of osmium tetrachloride. The tetrachloride was removed as before, and then the more volatile product was similarly removed but from the exit end of the tube. From 5.51 g. of consumed osmium was obtained 1.0 g. (10%) of osmium tetrachloride and 7.6 g. (77%) of diosmium oxide octachloride as red-brown crystals. Freshly prepared, it was soluble in petroleum ether, benzene, and ether, but it reacted readily with moist air to give insoluble material. The infrared spectrum showed a medium band at 10.02μ that disappeared on brief exposure of the sample to moist air.

Anal. Calc'd. for OsOCl_4 : Cl, 40.75; Os, 54.66; O, 4.59.
 Os_2OCl_8 : Cl, 41.70; Os, 55.92; O, 2.35.
Found: Cl, 41.65; Os, 55.97; O, 2.38.**

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- * This oxychloride was first obtained by chlorination of osmium with chlorine from a cylinder that evidently contained some air. When an attempt was made to remove the product under petroleum ether, the product dissolved. After four additional runs had given the soluble material, a sixth chlorination gave predominantly insoluble osmium tetrachloride with no apparent change of conditions, and three subsequent runs gave the tetrachloride in good yield. In an attempt to produce the oxychloride; conditions were restored to those of the original run, including the use of a fresh tank of chlorine. When the soluble material was indeed obtained, the original tank was then used; essentially, only osmium tetrachloride was obtained. The infrared spectra of the chlorine from the two tanks differed, in that the fresh chlorine showed the presence of carbon dioxide. However, bleeding carbon dioxide into the chlorine stream during chlorination did not give the soluble product, but when air was substituted for carbon dioxide, the oxychloride was obtained in good yield.

** By difference.

In a repeat run, the yield of OsCl_4 was 15% and of Os_2OCl_8 67%.

Thermal Decomposition of Diosmium Oxide Octachloride. Attempted sublimation of diosmium oxide octachloride* at 5 mm. at a bath temperature of 125°C gave a red-brown sublimate of osmium trichloride. It did not absorb in the infrared region.

Anal. Calc'd. for OsCl_3 : Cl, 35.87; Os, 64.13.
Found: Cl, 35.93; Os, 63.83.

Osmocene from Osmium Tetrachloride. Under a nitrogen stream, 5.46 g. (0.0238 mole) of sodium was added to 225 ml. of 1,2-dimethoxyethane** and followed by 24 ml. of cyclopentadiene. After the mixture was stirred 45 min. at room temperature and refluxed 2 hrs. without nitrogen flow, an additional 6 ml. of cyclopentadiene was added through the condensor and the mixture refluxed until the sodium was gone (30 min.). The colorless solution of cyclopentadienylsodium was cooled in an ice bath under a nitrogen stream, 18.2 g. (0.0548 mole) of powdered osmium tetrachloride was added in one portion (no heat evolution evident), and the mixture refluxed for 100 hrs. Solvent was removed in vacuo under nitrogen, the residue (pyrophoric) sublimed at $160^\circ\text{C}/0.1$ mm., and the sublimate resublimed at $120^\circ\text{C}/0.1$ mm. The product (2.35 g.) was crystallized from 13 ml. of toluene to give 2.17 g. (12%) of osmocene, m.p. $227.5\text{--}228^\circ\text{C}$ ***

When the reaction was run 22 hrs. instead of 100 hrs., yields of osmocene were 8%, 11%, and 13%, the lowest yield being obtained when the solvent was distilled from calcium hydride.

* The Os_2OCl_8 deliquesced during rapid transfer to a sublimation tube that had been filled with nitrogen. From an early chlorination at an unknown air to chlorine ratio, an oxychloride was obtained as a petroleum ether solution and was distilled. In addition to a crystalline sublimate, a small amount of liquid distillate was obtained that soon crystallized. An infrared spectrum of the distillate showed sharp peaks at 2.95μ (medium), 9.8μ (strong), 10.02μ (medium), and 10.5μ (weak). The spectrum differed, therefore, from that of Os_2OCl_8 . After two months at room temperature under nitrogen, the distillate no longer absorbed in the infrared.

** Freshly distilled into the reaction flask from lithium aluminum hydride under nitrogen.

*** Fischer and Grubert reported a 23% yield of osmocene, m.p. $229\text{--}230^\circ\text{C}$. They described the hot solution of cyclopentadienylsodium as violet, reported heat evolution on addition of crude osmium tetrachloride, and used chromatography on the twice-sublimed product (24).

Osmocene from Osmium Oxide Octachloride. When 18.2 g. (0.0268 mole) of Os_2OCl_8 was used in place of OsCl_4 with 0.238 mole of sodium in the preceding procedure, the yield of osmocene, m.p. 227-228°C, was 1.65 g. (10%). In an initial run, some Os_2OCl_8 was lost during addition because of the vigor of the reaction; the yield of material, m.p. 228-9°C, was 11%. To be correct, 0.238 mole of cyclopentadienylsodium should have been treated with 0.0238 mole of Os_2OCl_8 . These experiments were run before the identity of the oxychloride was known.

o-Methoxybenzoylosmocene (Crude). Powdered aluminum chloride (0.266 g.; 2.00 mmole) was added to a solution of 0.319 g. (1.87 mmole) of o-methoxybenzoyl chloride (freshly distilled) in 20 ml. of dry methylene chloride (freshly distilled from calcium hydride) in an ice bath under nitrogen, and the mixture was stirred 30 min. at room temperature. Osmocene (0.300 g.; 0.937 mmole) and 5 ml. of dry methylene chloride were added and the mixture refluxed for one week. It was poured into water, the aqueous layer extracted with chloroform, and the combined organic layers dried and taken to dryness. Chromatography of the residue (0.57 g.) in 6 ml. of benzene on 12 g. of alumina in petroleum ether gave 0.14 g. (47%) of osmocene by elution with petroleum ether and benzene and washing the eluted solid with a little petroleum ether. Subsequent elution with chloroform removed a yellow band of o-methoxybenzoylosmocene (45%, ca.). Extraction of the column with dilute base removed 0.16 g. (56%) of o-methoxybenzoic acid (infrared comparison). The crude osmocene derivative melted near 140°C with decomposition and the infrared spectrum bore a close resemblance to that of o-methoxybenzoylferrocene.

Anal. Calc'd. for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Os}$: C, 47.56; H, 3.55.
Found: C, 50.77; *H, 3.57.

From three earlier runs of less than 24-hrs. duration, recovery of osmocene was over 70%. In the initial run, none of the reagents were freshly purified; little (if any) o-methoxybenzoic acid was isolated, and recovery of osmocene was 86%. In the second run, the reagents were purified and the o-methoxybenzoyl chloride added to the osmocene and aluminum chloride in methylene chloride; recovery was 73%. In the third run, a solution of the complex of o-methylbenzoyl chloride and aluminum chloride was added to the osmocene in methylene chloride during a 7-hr. period; recovery, 72%.

In one instance the infrared spectrum of the recovered osmocene was missing a band at 11.4μ , but when the sample was sublimed, the sublimate then showed the 11.4μ band.

* The carbon value would be high if, during determination of carbon, osmium tetroxide sublimed into the carbon dioxide absorption tube. The analyst reported that he could not obtain a carbon analysis on o-hydroxybenzoyl-osmocene for this reason.

o-Hydroxybenzoylosmocene. Run 1. The preceding detailed procedure was applied to 6.15 g. of osmocene, m.p. 226-228°C, and granular aluminum chloride. However, some time after the mixture had refluxed 48 hrs. and before 110 hrs. had expired, the reaction mixture went to dryness. To the residue was added chloroform and water, the mixture stirred 2 hrs., and the layers separated. The organic layer (and one extract) was dried with magnesium sulfate, solvent removed in vacuo, and the residue (11.62 g.) dissolved in 125 ml. of benzene. Chromatography of the solution on 250 g. of alumina in petroleum ether by elution with petroleum ether and benzene and sublimation of the eluted solid gave 1.91 g. (31%) of recovered osmocene, m.p. 225-226.5°C. Recrystallization from 6.5 ml. of toluene gave 1.79 g., m.p. 227-230.5°C. Subsequent elution with chloroform and ether was ineffective, but 3:1 chloroform-methanol removed 3.18 g. of material. The column was extracted with a mixture of 5% aqueous sodium hydroxide and chloroform, the aqueous layer extracted with chloroform, and the combined organic layers dried and taken to dryness. The residue, 1.15 g., was combined with the 3.18 g. and the mixture stirred in 50 ml. of 6% sodium hydroxide overnight. After the mixture was heated to dissolve solids present, it was filtered through Celite wet with hot 6% sodium hydroxide, washed with hot 6% base, and the filtrate cooled. Extraction of the basic filtrate with chloroform and evaporation of the dried extract to dryness left 3.06 g. of yellow crystals, which when crystallized from ether with filtration furnished 2.15 g. (25%) of crude o-hydroxybenzoylosmocene, m.p. 94-96°C. Chromatography on Florisil in petroleum ether by elution with ether and washing the eluted solid with benzene yielded 0.39 g. of material, m.p. 99-100°C, and from the filtrate 1.37 g., m.p. 98-99°C. The latter was analyzed.

Anal. Calc'd. for $C_{17}H_{14}O_2Os$: C, 46.35; H, 3.20; Os, 43.18.
Found: * C, 46.46; H, 3.48; Os, 43.41.

Run 2. Granular aluminum chloride (4.04 g.; 0.0302 mole) was added to 4.57 g. (0.0268 mole) of o-methoxybenzoyl chloride (from a new bottle; not freshly distilled) in 275 ml. of dry methylene chloride and the mixture stirred 3.5 hrs. Osmocene (4.27 g.; 0.0133 mole) was added, the mixture was refluxed 24 hrs. under nitrogen, and the gum that crystallized during this time was broken up. The refluxing was continued for 65 hrs. more, solvent was then removed by distillation in a hot water bath, and the residue was kept in a 90° bath for 5.5 hrs. After the mixture was cooled, chloroform and water were added to the residue, the mixture was stirred for 2 hrs., and the layers were separated. After solvent was removed from the organic layer and one extract, the residue (9.13 g.) was dissolved in 55 ml. of chloroform, the solution chromatographed on Florisil in petroleum ether by elution with petroleum ether, benzene, and 1:1 benzene-ether, and the eluted material crystallized from toluene to give 2.78 g. (67%) of recovered osmocene, m.p. 227-228°C. Elution

* Schwartzkopf Microanalytical Laboratory.

with ether gave 0.82 g. and with 3:1 chloroform-methanol 1.45 g., while extraction of the column with a mixture of 5% sodium hydroxide and chloroform furnished 0.58 g. of additional material (from the organic layer). The three fractions were each stirred overnight in 6% sodium hydroxide, filtered hot through Celite, and the basic filtrates extracted with chloroform. Removal of solvent from the extracts gave a total of 1.42 g. (24%) of very crude o-hydroxybenzoylosmocene.

Unsuccessful Reactions with Osmium Chlorides Containing Oxygen. "Anhydrous osmium trichloride" (62.7% Os) purchased from Engelhard Industries, Inc., 113 Astor St., Newark 2, N. J., was found to contain a 1 to 1 ratio of oxygen to osmium.* Thus, when 25.1 g. of the material was heated in an argon stream at temperatures up to 375°C, a small amount of water was evolved, and at 500°C, when the argon was briefly turned off, gas evolution was noted. After 17 hrs. at 500°C, the residue weighed 19.3 g. and the amount of sublimate was small. The infrared spectrum of the residue, $(Os_2Cl_3O_2)_n$, showed a peak at 8.9μ (Os-O) with no hydroxyl absorption.

Anal. Calc'd. for $Os_2Cl_3O_2$: Cl, 20.51; Os, 73.32; O, 6.17.
Found: Cl, 20.74; Os, 72.92; O, 6.34.**

From this result, the starting "anhydrous osmium trichloride" apparently had an O to Os ratio of 1 or more. The material showed broad infrared bands at 3μ (hydroxyl), 9μ , and 9.8μ (Os-O) that were unchanged after the sample was heated 20 hrs. at 330°C at 0.03-0.15 mm. The composition of this material was not established, but it may have been $Os_4Cl_{11}H_5O_4$, which by the loss of 5HCl yielded $2Os_2Cl_3O_2$ ***

Anal. Calc'd. for $OsCl_3$: Cl, 35.87; Os, 64.1; O, 0.00.
 $Os_4Cl_{11}H_5O_4$: Cl, 31.8; Os, 62.6; O, 5.6.
Found: Cl, 32.37; Os, 62.7; O, 4.9.**

* An earlier lot apparently contained 50% or more osmium tetrachloride (2).

** By difference.

*** The supplier stated that the material was prepared from ammonium hexachlorosmate (38) (42.8% Os; calc'd. for $(NH_4)_2(OsCl_6)$, 43.3% Os) by chlorination with dry chlorine at 350°C, and that care was taken to avoid contact with air inasmuch as $OsCl_3$ is extremely hygroscopic. We are grateful to Engelhard Industries, Inc. for providing this information.

The following reactions were run under the erroneous assumption that the commercial "anhydrous osmium trichloride" was OsCl_3 and the product from its thermal decomposition was OsCl_2 . In view of the above results, they are reported here as reactions of $\text{Os}_4\text{Cl}_{11}\text{H}_5\text{O}_4$ and of $\text{Os}_2\text{Cl}_3\text{O}_2$, respectively.

1. Osmocene from $\text{Os}_4\text{Cl}_{11}\text{H}_5\text{O}_4$. Cyclopentadienylsodium prepared from 0.547 mole of sodium was treated with 50.0 g. of $\text{Os}_4\text{Cl}_{11}\text{H}_5\text{O}_4$ as described above for the preparation of osmocene from OsCl_4 . Sublimation of the dried reaction mixture residue gave only a trace of osmocene. In a second run, the osmium compound employed had been dried at 330°C at 0.03-0.15 mm. for 20 hrs., but the yield of osmocene was again negligible. The sublimation residue from the second run was heated at 450°C for 5 hrs. under a slow nitrogen flow; only a small amount of dark powder sublimed.

A mixture of 2.0 g. of $\text{Os}_4\text{Cl}_{11}\text{H}_5\text{O}_4$ in 18.4 ml. (20 mmole) of 1.09 N bis(cyclopentadienyl)-magnesium (39) in toluene was stirred 2.5 hrs. at room temperature and then refluxed overnight in a slow stream of nitrogen. The hot solution was filtered, the filtrate treated with water (considerable heat evolved), and the organic layer dried and taken to dryness. The residual yellow oil weighed 0.1 g.

2. Osmocene from $\text{Os}_2\text{Cl}_3\text{O}_2$. Treatment of cyclopentadienylsodium (from 0.05 mole of sodium) in 50 ml. of dry dimethoxyethane with 6.5 g. of $\text{Os}_2\text{Cl}_3\text{O}_2$ as described for OsCl_4 (24) gave 0.02 g. of osmocene after one sublimation.

3. Osmocene from $\text{OsCl}_4 \cdot \text{OsCl}_3 \cdot 7\text{H}_2\text{O}$. Before osmium trichloride purchased from D. F. Goldsmith Chemical and Metal Corp. was identified as hydrated material, it was employed in a reaction with bis(cyclopentadienyl)-magnesium in toluene and with cyclopentadienylsodium in 1,2-dimethoxyethane. In neither case was osmocene isolated.

F. Ruthenocene Derivatives

Ruthenocene. (1) From cyclopentadienylsodium. Cyclopentadienylsodium from 0.624 g. atom of sodium was stirred with 29.2 g. (0.140 mole) of ruthenium trichloride in refluxing dimethoxyethane for 117 hrs. to give 4.0 g. (12%) of ruthenocene, m.p. 200°C . The method employed was essentially that of Fischer and Grubert (24), who reported a 52% yield, m.p. 200°C . A longer heating time was employed here as suggested by the work of Bublitx, et al. (40). In a second run in which drier solvent was employed, the yield from 0.64 g. atom of sodium and 0.157 mole of ruthenium trichloride was 21%.

(2) From bis(cyclopentadienyl)-magnesium. Treatment of cyclopentadiene in toluene with methylmagnesium iodide in ether, removal of solvent, and sublimation of the residue furnished bis(cyclopentadienyl)-magnesium, which was stored as a 0.125-M solution in toluene. A mixture of 57.5 ml. (7.2 mmole) of the solution and 1.0 g. (4.8 mmole) of ruthenium trichloride was refluxed under

nitrogen for 48 hrs., cooled, and filtered. The filtrate and one wash was treated with 8 ml. of 5% aqueous sodium hydroxide, and the organic layer was taken to dryness. Chromatography of the residue (0.2 g.) on alumina yielded 0.07 g. (6%) of ruthenocene, identified by infrared comparison.

o-Hydroxybenzoylruthenocene. o-Methoxybenzoylruthenocene. To 0.74 g. (4.34 mmole) of o-methoxybenzoyl chloride in 50 ml. of dry methylene chloride (freshly distilled from calcium hydride) was added about 0.58 g. (4.34 mmole) of granular aluminum chloride and the mixture stirred under nitrogen for 1.5 hrs. Ruthenocene (1.0 g.; 4.34 mmole) was added in one portion, the mixture was refluxed for 48 hrs., and the solvent then removed by a hot water bath. The residue was kept in a bath at 90-95°C for 18 hrs., cooled, and a mixture of 25 ml. of water and 15 ml. of chloroform was added. After the mixture was stirred for 2 hrs. under nitrogen, the organic phase and one chloroform wash of the aqueous layer were dried and the solvent removed. Chromatography of the residue in chloroform on 30 g. of Florisil in petroleum ether by elution with petroleum ether, benzene, ether, and 3:1 chloroform-methanol gave fractions of 0.1 g., 1.6 g., 0.5 g., and 0.5 g., respectively. Combination of the first two fractions and similar chromatography on alumina yielded 0.2 g. (13%) of o-methoxybenzoylruthenocene, m.p. 142-143°C, from a benzene fraction. When elution with ether failed to remove a second band, the alumina column was extracted with a mixture of chloroform and 5% sodium hydroxide solution, the basic layer extracted with chloroform, and the combined organic layers dried and taken to dryness to give 0.3 g. (20%) of o-hydroxybenzoylruthenocene, m.p. 92-93°C.

Anal. Calc'd. for $C_{17}H_{14}O_2Ru$: C, 58.01; H, 4.01; Ru, 28.89.

Found: C, 58.27; H, 4.09; Ru, 29.15.

The 0.5-g. ether fraction from the chromatography on Florisil was chromatographed on alumina to give 0.258 g. (16%) of o-methoxybenzoylruthenocene, m.p. 143-144°C (shrinks 141°C).

Anal. Calc'd. for $C_{18}H_{16}O_2Ru$: C, 59.06; H, 4.41; Ru, 27.79.

Found: C, 59.34; H, 4.64; Ru, 27.50.

By extraction of the second alumina column with chloroform-base, 0.200 g. (13%) of crude o-hydroxybenzoylruthenocene was obtained. Attempts to isolate additional hydroxy compound from the 0.5-g. chloroform-methanol fraction and by extraction of the Florisil column with chloroform-base did not yield a significant amount of material soluble in aqueous sodium hydroxide. In summary, the yields of methoxy and crude hydroxy compounds were 29% and 33%, respectively. The infrared spectra compared well with those of the ferrocene and osmocene analogs.

G. Spectra and Physical Properties

Ultraviolet and visible spectra were determined locally by Arthur Raymond on a Perkin-Elmer Spectracord Model 4000 and a Beckman Model DU Quartz Spectrophotometer. Infrared spectra were obtained with a Baird Infrared Recording Spectrophotometer.

TABLE II

ABSORPTION SPECTRAL DATA FOR o-HYDROXYBENZOYLRUTHENOCENE IN CYCLOHEXANE

Concn.: 4.77×10^{-5} M					
λ	$\% T$	$\log \epsilon$			
200	5.1	4.55	325	56.1	3.72
215	10.1	4.32	330	54.1	3.75
220	14.5	4.25	335	52.2	3.77
225	26.9	4.08	340	52.4	3.76
230	34.5	3.99	345	53.8	3.75
235	41.2	3.91	350	55.6	3.73
240	47.5	3.83	360	59.0	3.68
245	50.0	3.80	370	65.3	3.59
250	43.9	3.88	380	71.0	3.49
255	36.0	3.97	390	75.7	3.40
258	33.5	4.00	400	80.7	3.29
260	34.1	3.99			
265	35.6	3.97			
270	35.8	3.97			
275	36.7	3.96			
280	40.8	3.91			
285	48.2	3.82			
290	59.9	3.67			
300	71.8	3.48			
310	66.9	3.56			
320	59.4	3.68			

Concn.: 2.38×10^{-5} M		
λ	$\% T$	$\log \epsilon$
410	1.4	2.89
420	13.6	2.56
430	39.1	2.23
440	62.9	1.93
450	78.6	1.64
460	89.4	1.31

TABLE III

ABSORPTION SPECTRAL DATA FOR o-HYDROXYBENZOYLISMOCENE IN CYCLOHEXANE

Concn.: 3.64×10^{-5} M					
λ	ϵ	$\log \epsilon$			
218	23.2	4.24	325	62.7	3.75
220	28.9	4.17	330	61.0	3.77
225	45.0	3.98	335	59.4	3.79
230	50.5	3.91	340	60.4	3.78
235	52.9	3.88	345	62.0	3.76
240	53.5	3.87	350	64.3	3.72
245	51.6	3.90			
250	48.7	3.94	Concn.: 4.045×10^{-4} M		
255	45.5	3.97	λ	ϵ	$\log \epsilon$
257	45.2	3.97	350	0.8	3.71
258	45.0	3.98	360	3.3	3.57
259	44.9	3.98	370	7.0	3.46
260	45.4	3.97	380	8.9	3.42
265	47.6	3.95	390	10.2	3.39
270	54.5	3.86	395	12.2	3.35
275	64.1	3.72	400	15.4	3.30
280	78.1	3.47	410	22.1	3.21
285	90.0	3.09	420	33.9	3.06
290	93.0	2.94	430	52.4	2.84
295	90.8	3.06	440	72.5	2.54
300	86.7	3.24	450	87.9	2.13
305	81.9	3.38	460	95.5	1.69
310	77.1	3.49	470	98.6	1.18
315	71.5	3.60	480	99.5	0.73
320	66.9	3.68			

TABLE IV
PHYSICAL CHARACTERISTICS OF CANDIDATE COMPOUNDS

Name	M.P., °C	Decompn. Temp., °C ^a	Color and Appearance	Soluble in			
				Ethanol	Methyl Ethyl Ketone	Ethyl Acetate	Benzene
Ruthenocene	197-200 ^c	>250	Pale yellow leaflets	--	1 $\frac{1}{2}$	1 $\frac{1}{2}$	3 $\frac{1}{2}$
<u>o</u> -Methoxybenzoyl- ruthenocene	143-144	>250	Yellow prisms	1 $\frac{1}{2}$	3 $\frac{1}{2}$	3 $\frac{1}{2}$	3 $\frac{1}{2}$
<u>o</u> -Hydroxybenzoyl- ruthenocene	92-93	>250	Yellow crystals	1 $\frac{1}{2}$	3 $\frac{1}{2}$	3 $\frac{1}{2}$	3 $\frac{1}{2}$
<u>o</u> -Hydroxybenzoyl- osmocene	99-100	200 ^d	Yellow prisms	1 $\frac{1}{2}$	3 $\frac{1}{2}$	3 $\frac{1}{2}$	3 $\frac{1}{2}$

^a Temperature at which a sample in a melting point capillary darkened significantly or evolved gas.

^b Compounds which did not dissolve at the 3 $\frac{1}{2}$ level were tested at the 1 $\frac{1}{2}$ level.

^c Lit. (24) m.p. 200°C.

^d Darkens above 200°C.

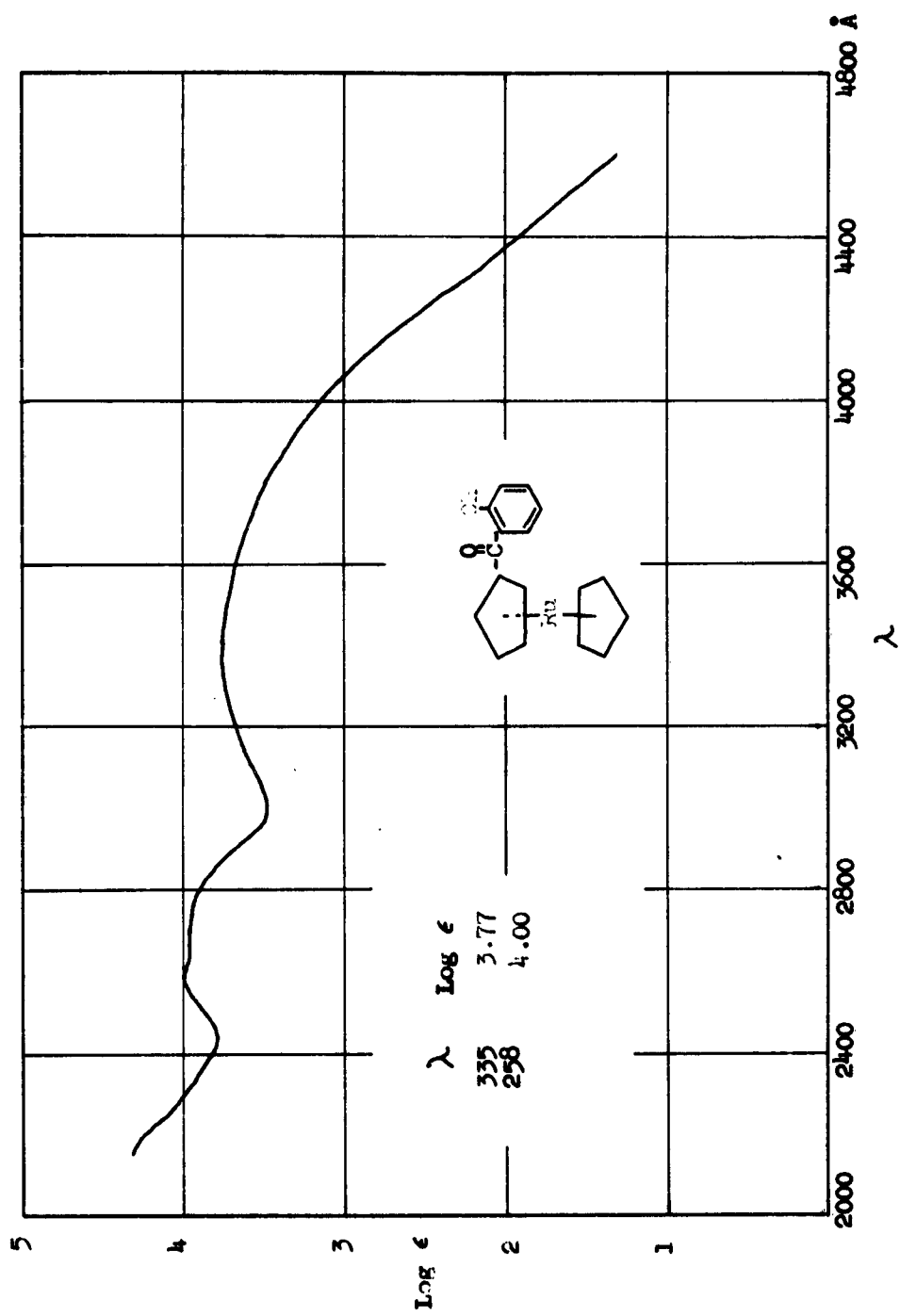


Figure 2. Absorption Spectrum of o-Hydroxybenzylruthenocene in Cyclohexane.

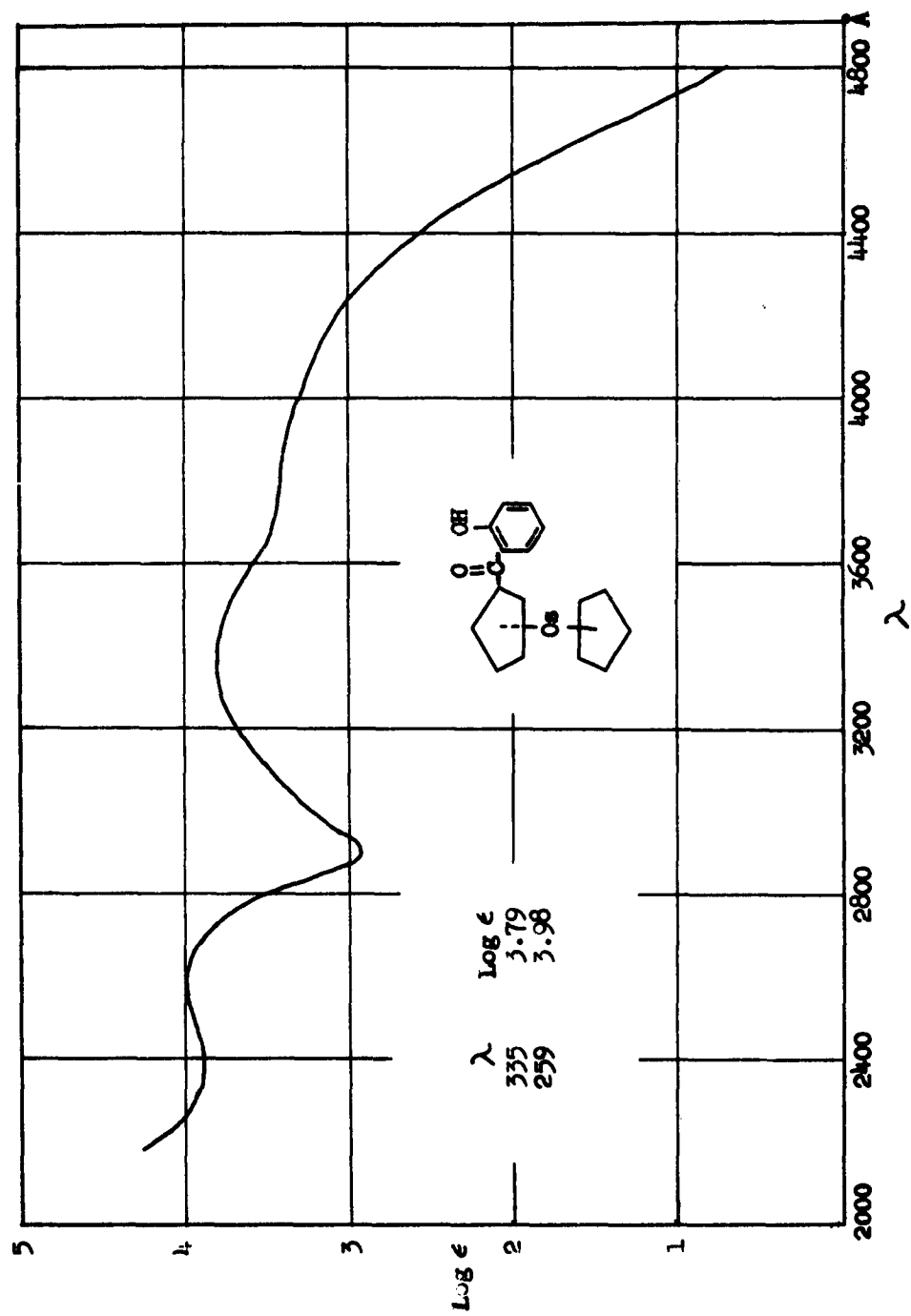


Figure 3. Absorption Spectrum of *o*-Hydroxybenzoylcamphene in Cyclohexane.

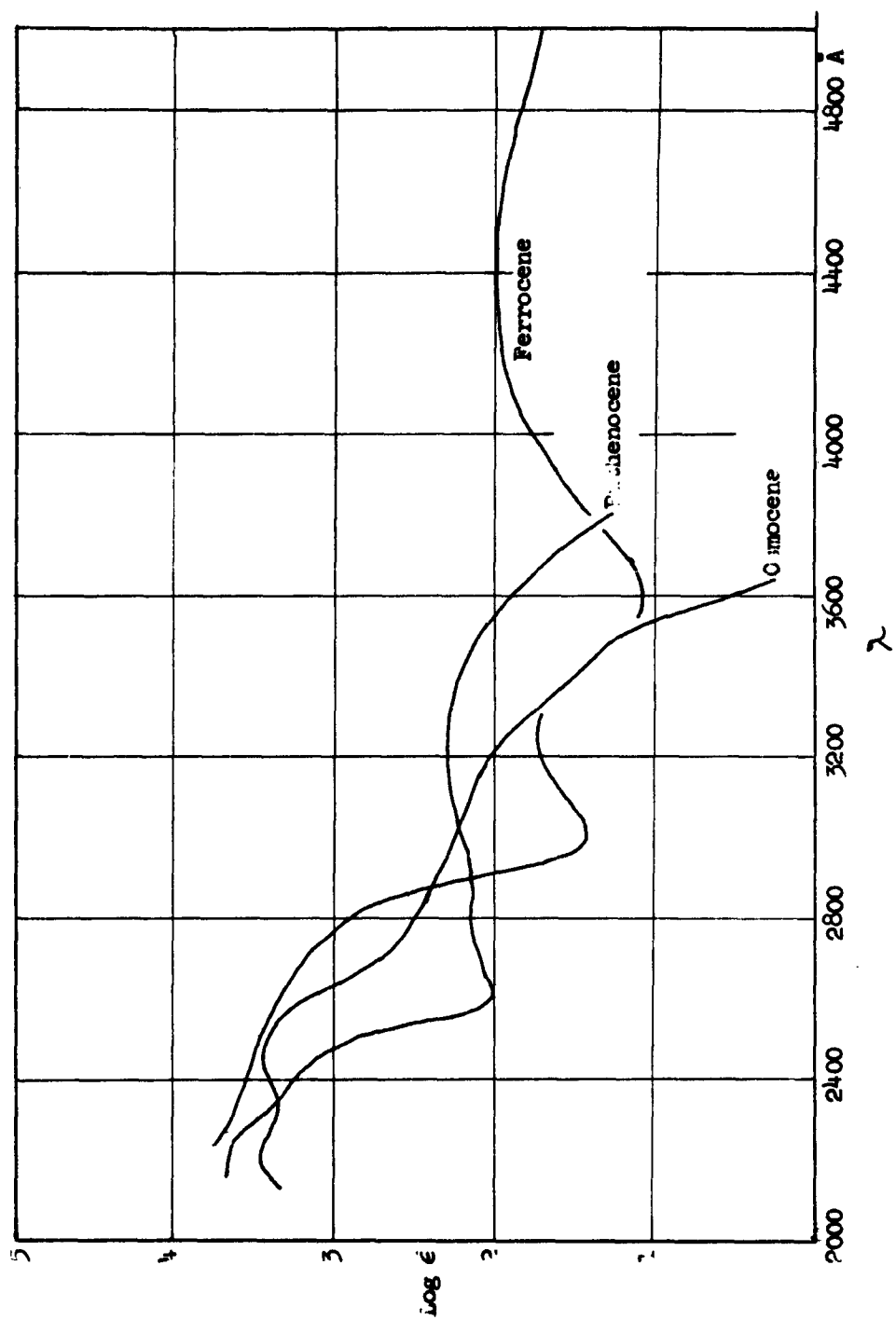


Figure 4. Absorption spectra of Ruthenocene and Osmocene in Cyclobexane and of Ferrocene in Ethanol.

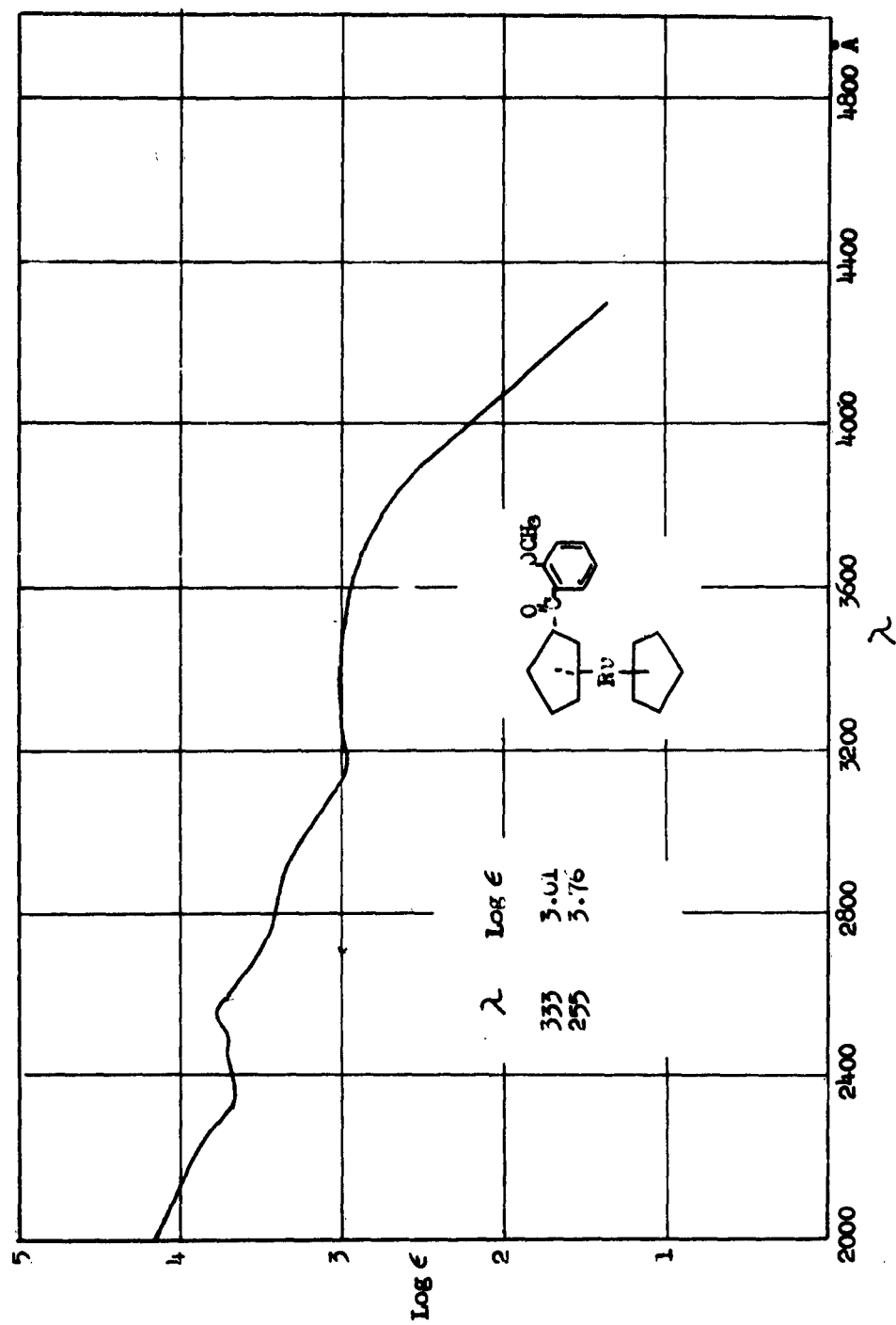


Figure 5. Absorption Spectrum of *o*-Methoxybenzoylruthenocene in Cyclohexene.

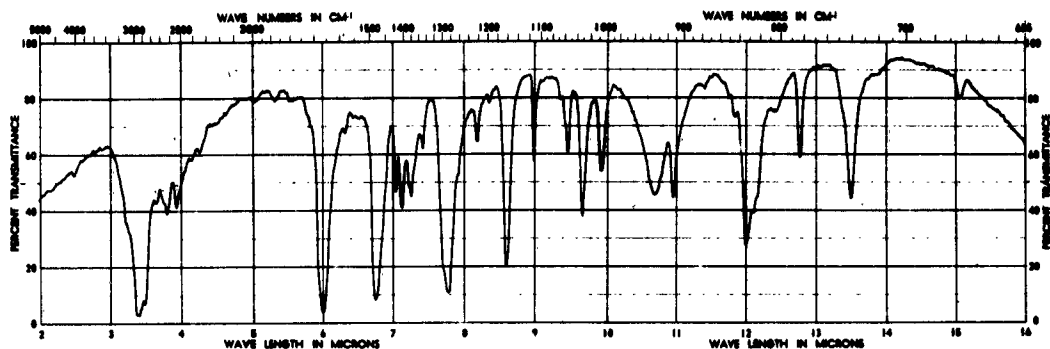


Figure 6. Infrared Spectrum of Ferrocenemonocarboxylic Acid (M.P. 224-225°C, dec.) in Nujol Mull.

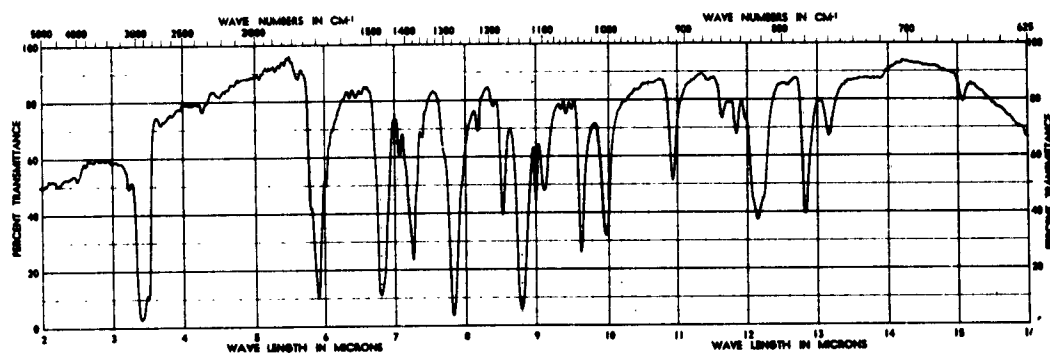


Figure 7. Infrared Spectrum of Ethyl Ferrocenemonocarboxylate (M.P. 63-64°C) in Nujol Mull.

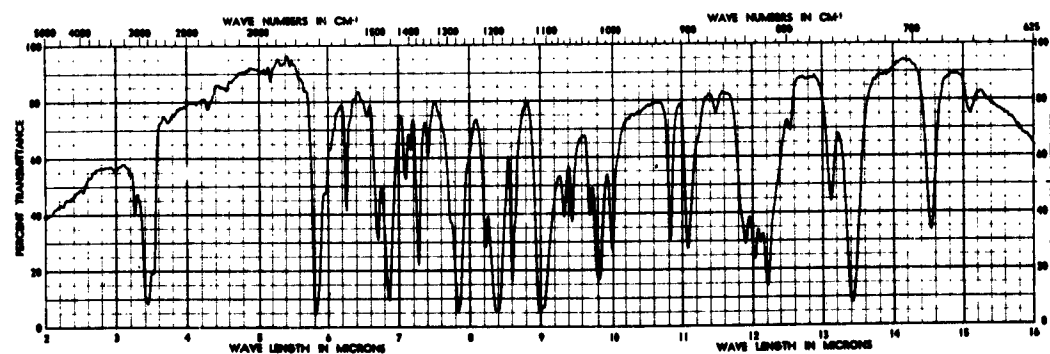


Figure 8. Infrared Spectrum of Phenyl Ferrocenecarboxylate (M.P. 124-124.5°C) in Nujol Mull.

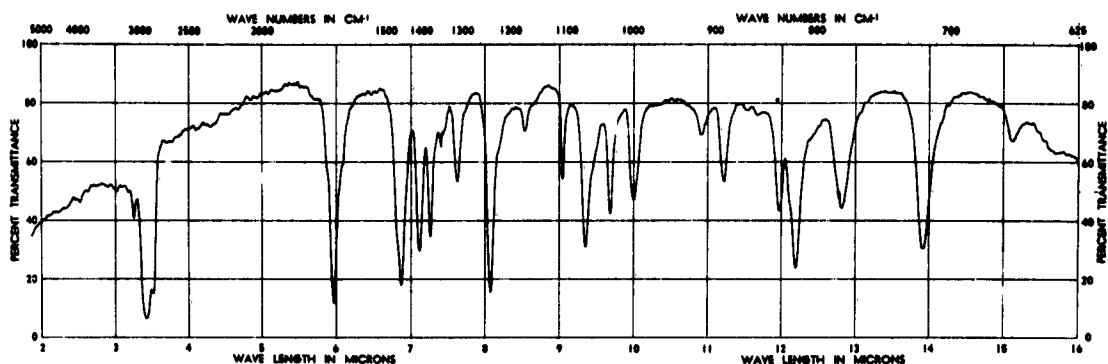


Figure 9. Infrared Spectrum of Chloroacetylferrocene (M.P. 90-91°C) in Nujol Mull.

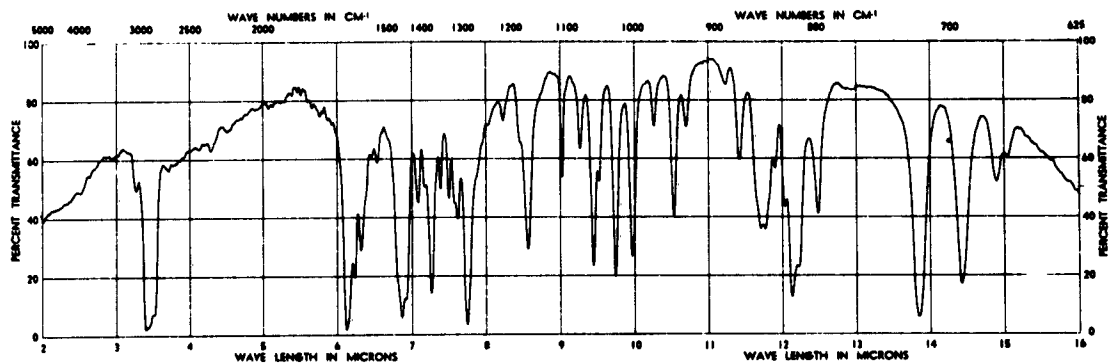


Figure 10. Infrared Spectrum of Benzoylferrocene (M.P. 108-108.5°C) in Nujol Mull.

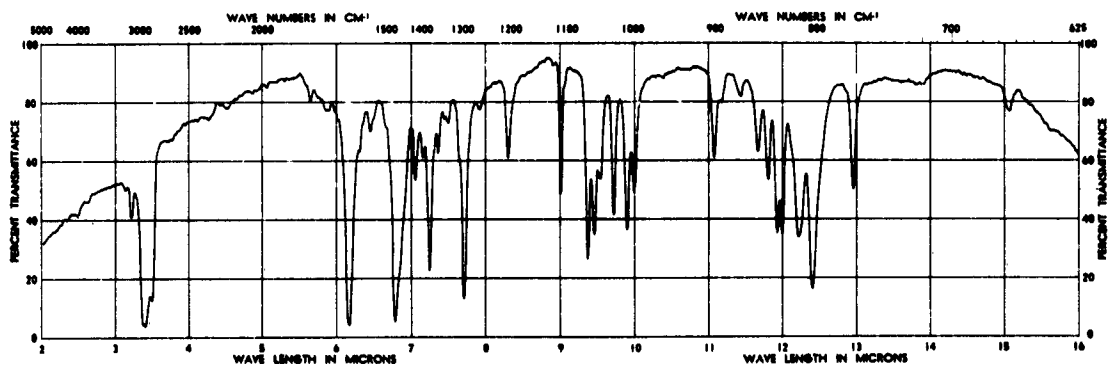


Figure 11. Infrared Spectrum of Diferrocenyl Ketone (M.P. 209.5-210°C) in Nujol Mull.

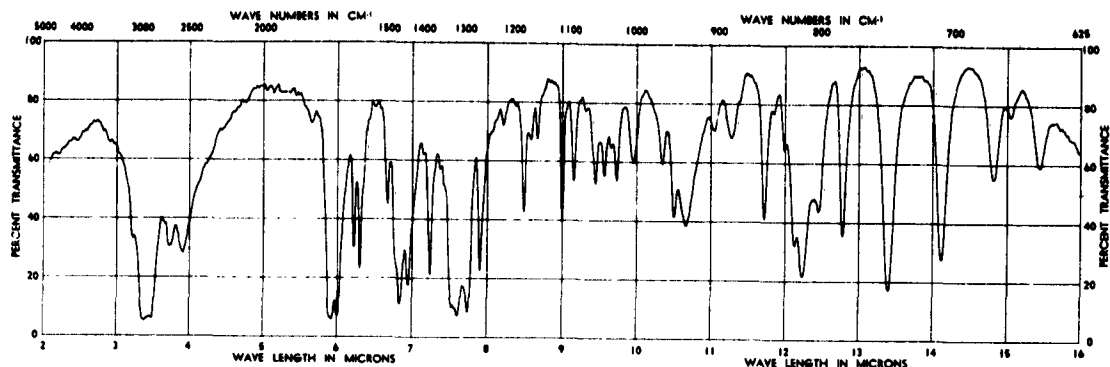


Figure 12. Infrared Spectrum of *o*-Carboxybenzoylferrocene (M.P. 190-195°C, dec.) in Nujol Mull.

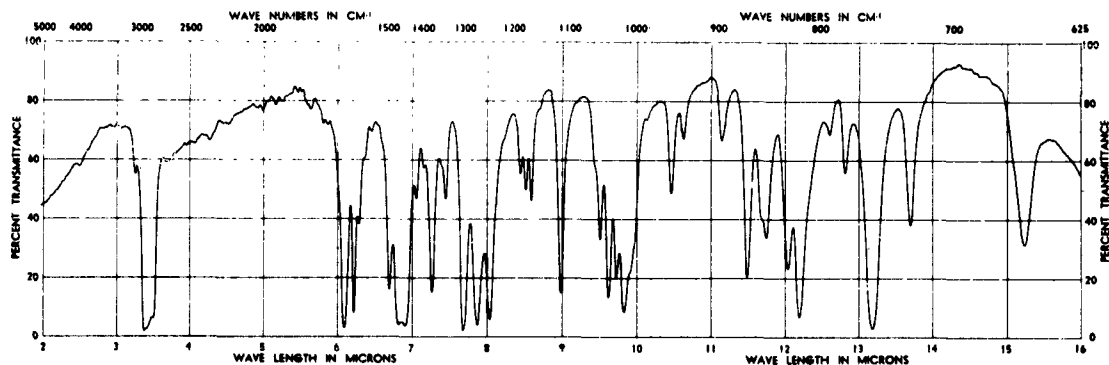


Figure 13. Infrared Spectrum of 2-Methoxybenzoylferrocene (M.P. 136-137°C) in Nujol Mull.

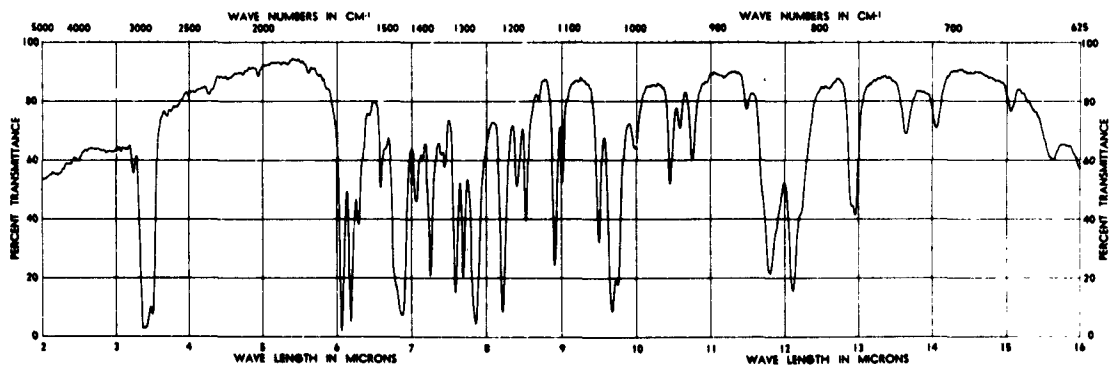


Figure 14. Infrared Spectrum of 2,4-Dimethoxybenzoylferrocene (M.P. 133.5-134°C) in Nujol Mull

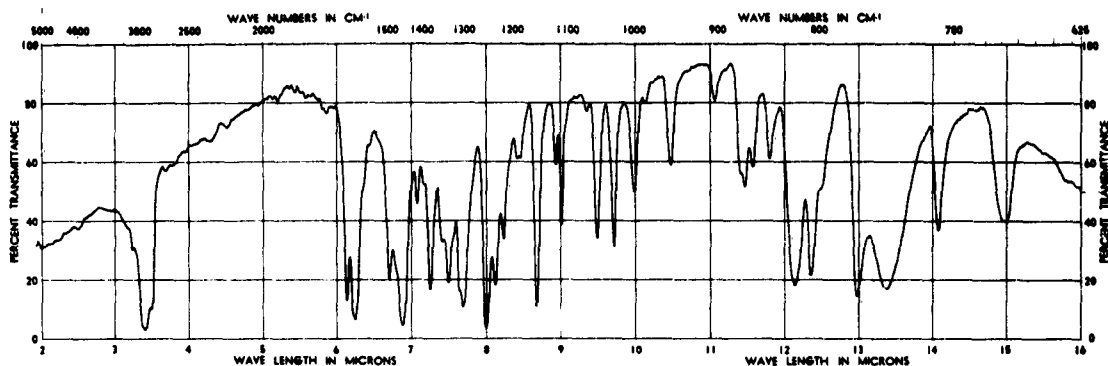


Figure 15. Infrared Spectrum of 2-Hydroxybenzoylferrocene (M.P. 87.5-88°C) in Nujol Mull.

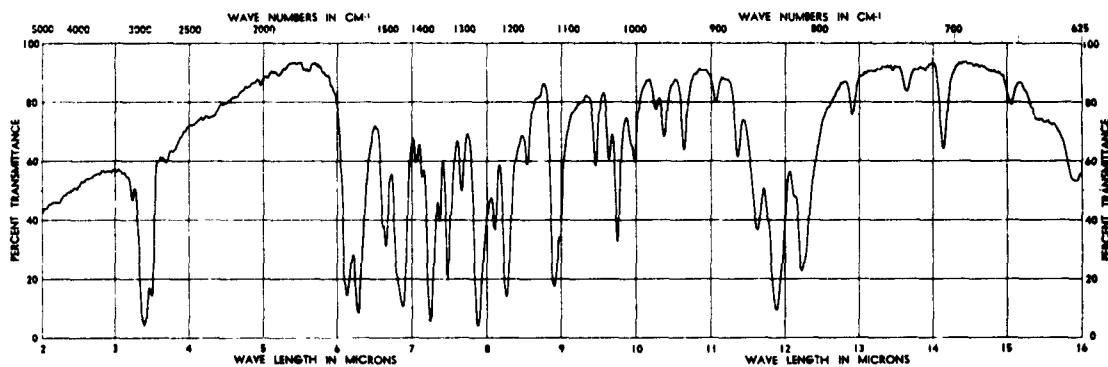


Figure 16. Infrared Spectrum of 2-Hydroxy-4-methoxybenzoylferrocene (M.P. 124.5-126°C) in Nujol Mull.

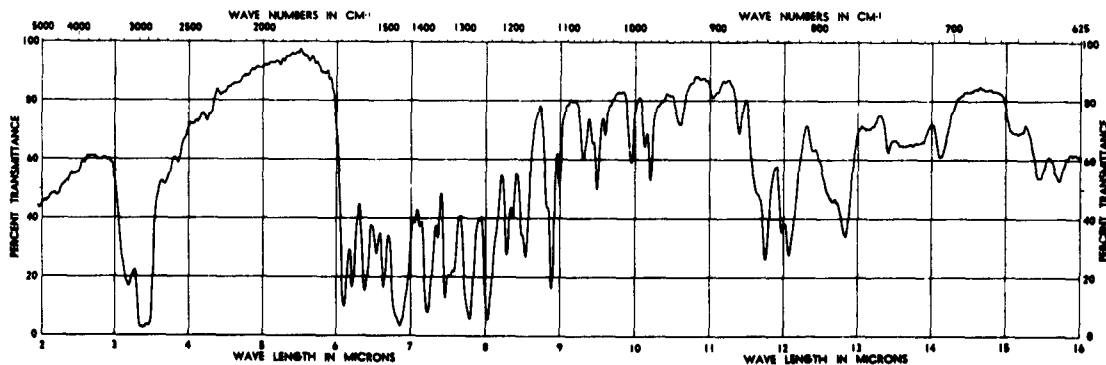


Figure 17. Infrared Spectrum of 2,4-Dihydroxybenzoylferrocene (M.P. 176-177°C) in Nujol Mull.

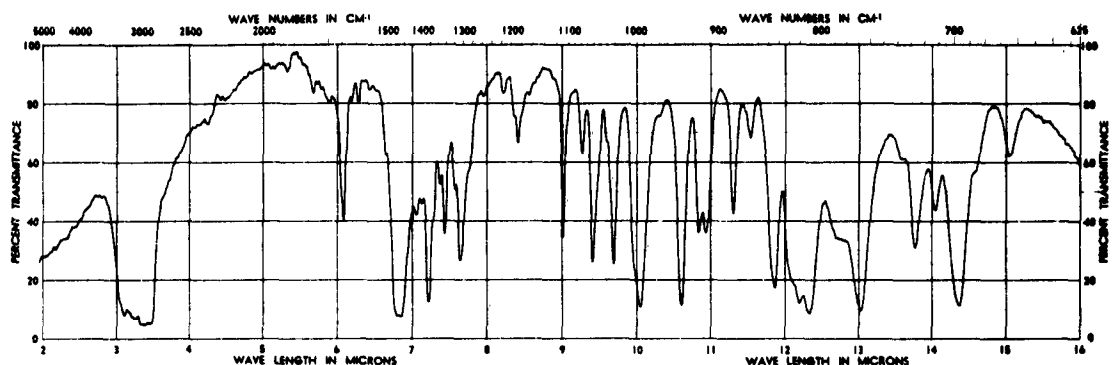


Figure 18. Infrared Spectrum of Benzoylferrocene Oxime (M.P. 161-162.5°C, dec.) in Nujol Mull.

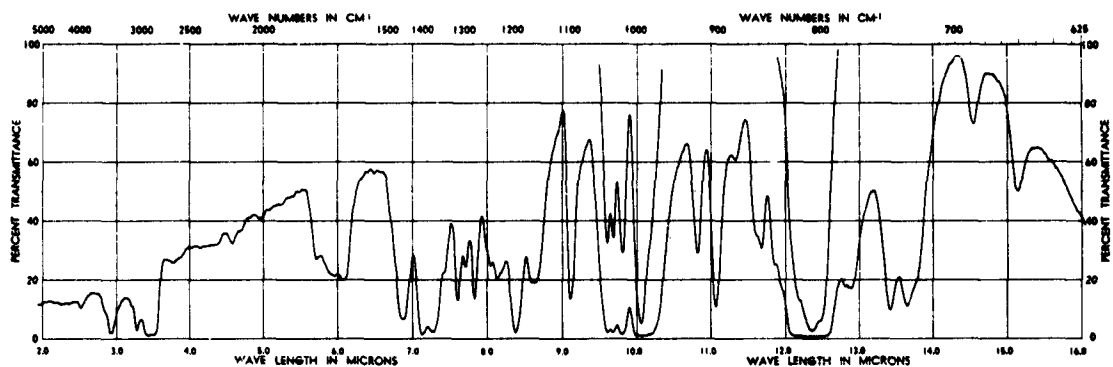


Figure 19. Infrared Spectrum of Diferrocenylmethanol (M.P. 173-175°C, dec.) in Nujol Mull.

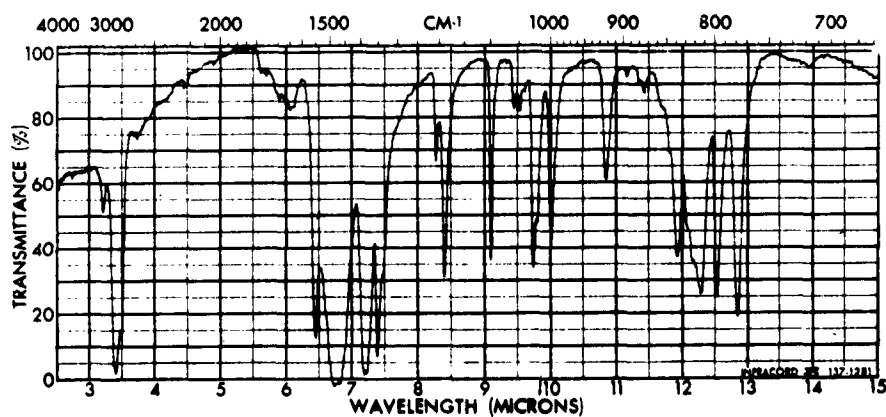


Figure 20. Infrared Spectrum of Ferrous Ferrocenoate in Nujol Mull.

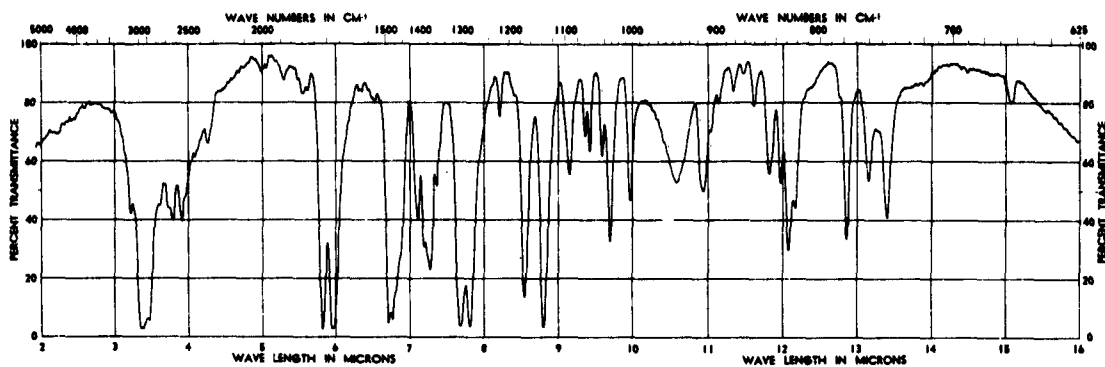


Figure 21. Infrared Spectrum of 1-Carboxy-1'-carbethoxyferrocene (M.P. 144-145°C) in Nujol Mull.

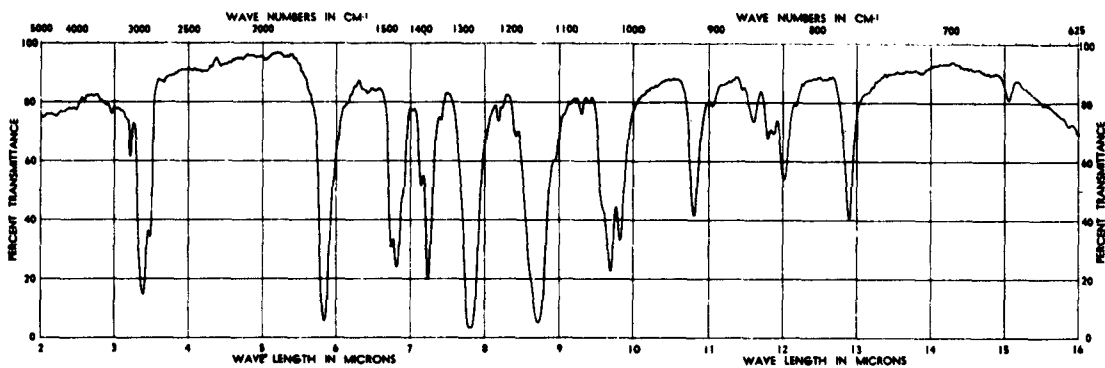


Figure 22. Infrared Spectrum of Diethyl 1,1'-ferrocenedicarboxylate (M.P. 41.5-42°C) in Nujol Mull.

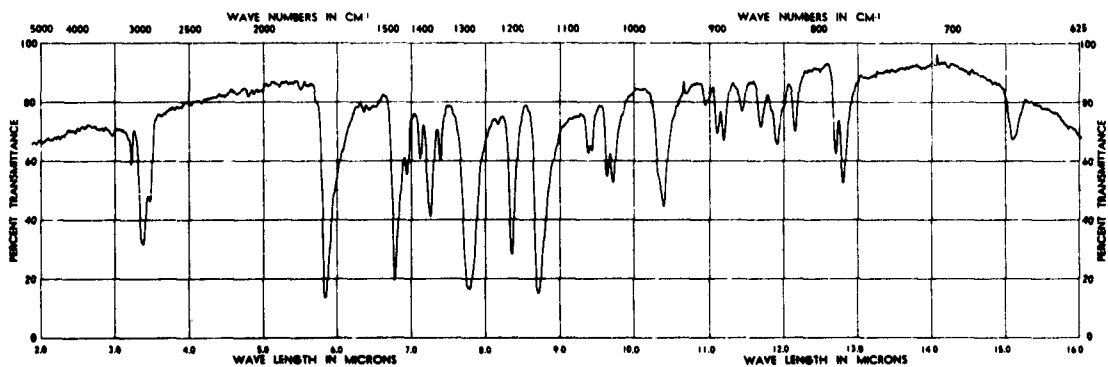


Figure 23. Infrared Spectrum of Dimethyl 1,1'-ferrocenedicarboxylate (M.P. 113.5-114.5°C) in Nujol Mull.

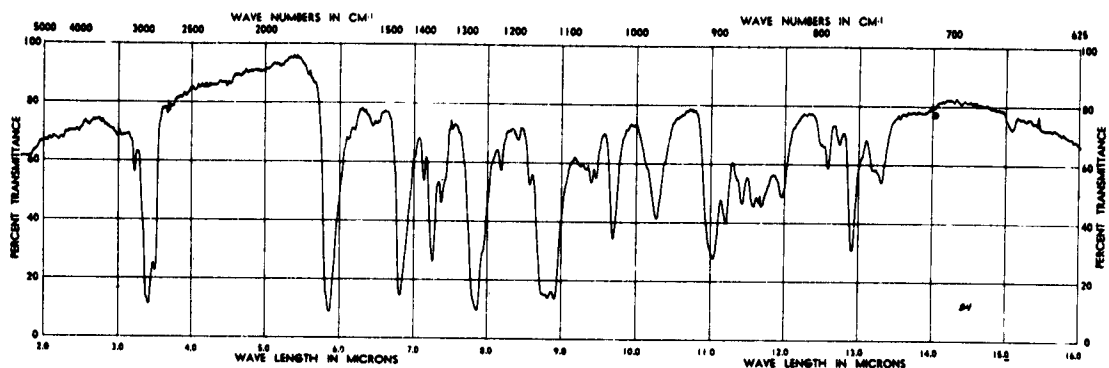


Figure 24. Infrared Spectrum of Bis(2,3-epoxypropyl) 1,1'-Ferrocene-dicarboxylate (M.P. 52-53°C) in Nujol Mull.

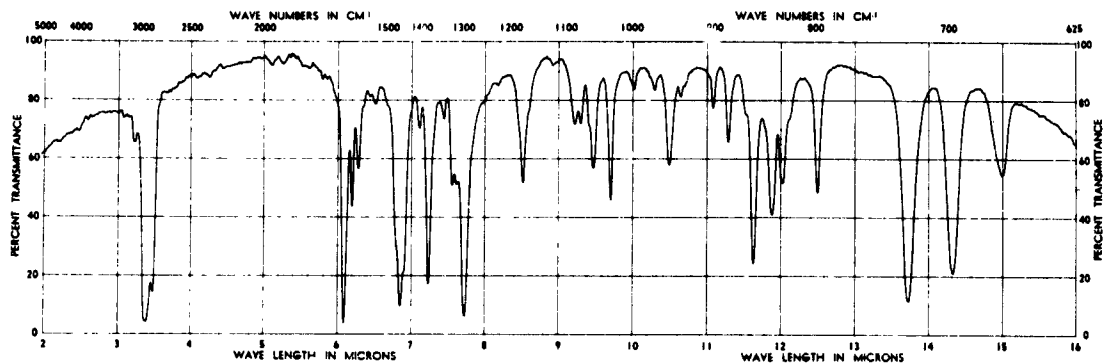


Figure 25. Infrared Spectrum of 1,1'-Dibenzoylferrocene (M.P. 104-105°C) in Nujol Mull.

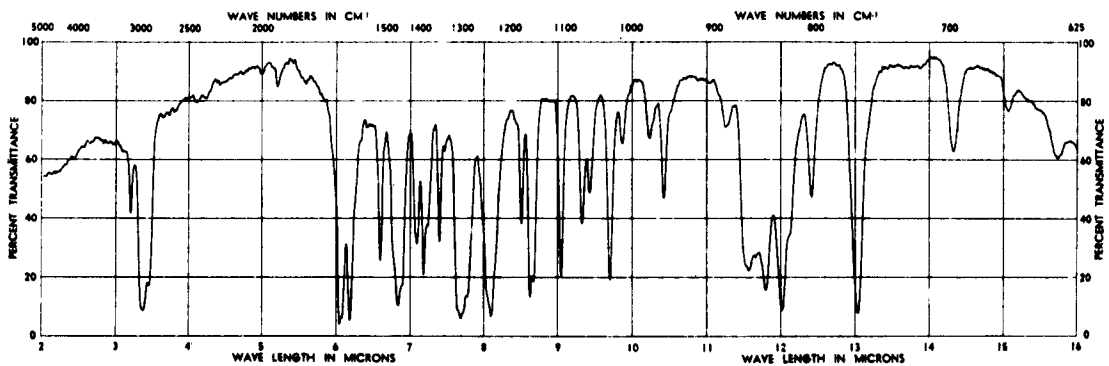


Figure 26. Infrared Spectrum of 1,1'-Bis(p-fluorobenzoyl)-ferrocene (M.P. 129-130.5°C) in Nujol Mull.

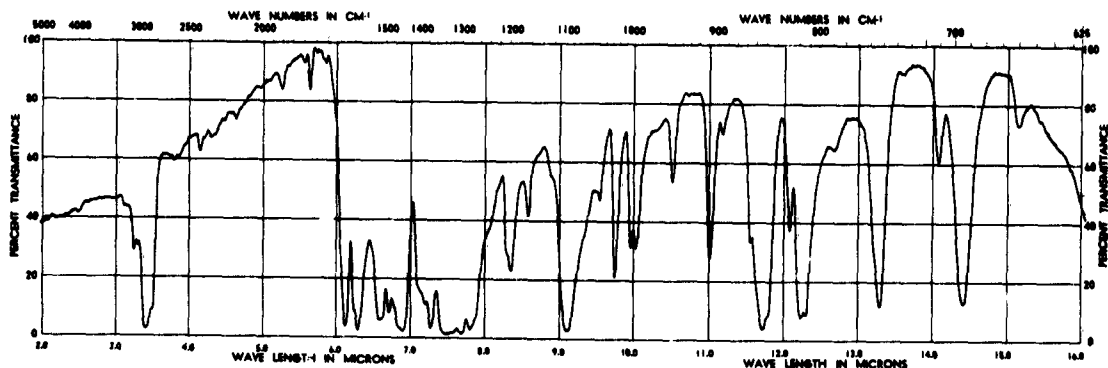


Figure 27. Infrared Spectrum of 1,1'-Bis[N-methyl-N-(p-nitrophenyl)-carboxamido]-ferrocene (M.P. 230-232°C, dec.) in Nujol Mull.

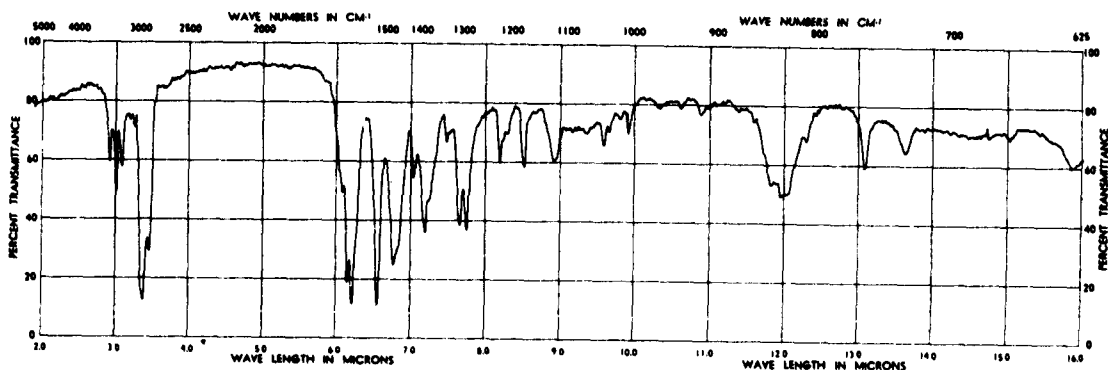


Figure 28. Infrared Spectrum of 1,1'-Bis[N-methyl-N-(p-nitrophenyl)-carboxamido]-ferrocene (M.P. 230-232°C, dec.) in Nujol Mull.

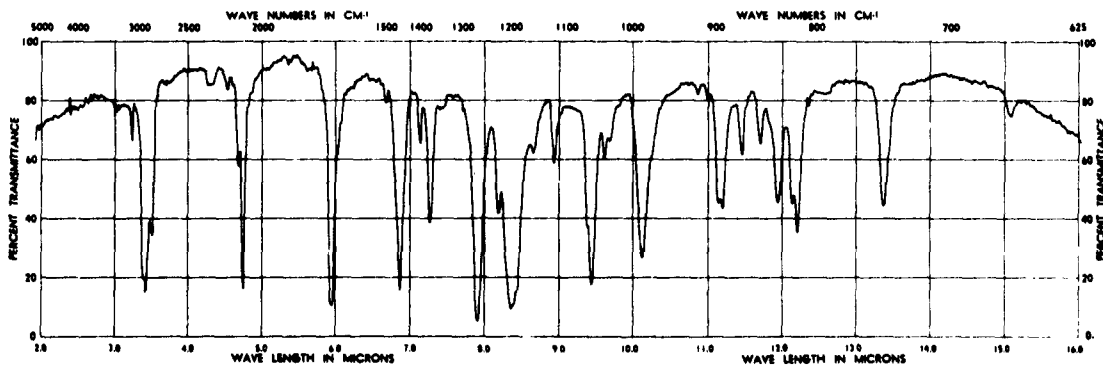


Figure 29. Infrared Spectrum of 1,1'-Dicarbazidoferrrocene (M.P. 115°C, dec.) in Nujol Mull.

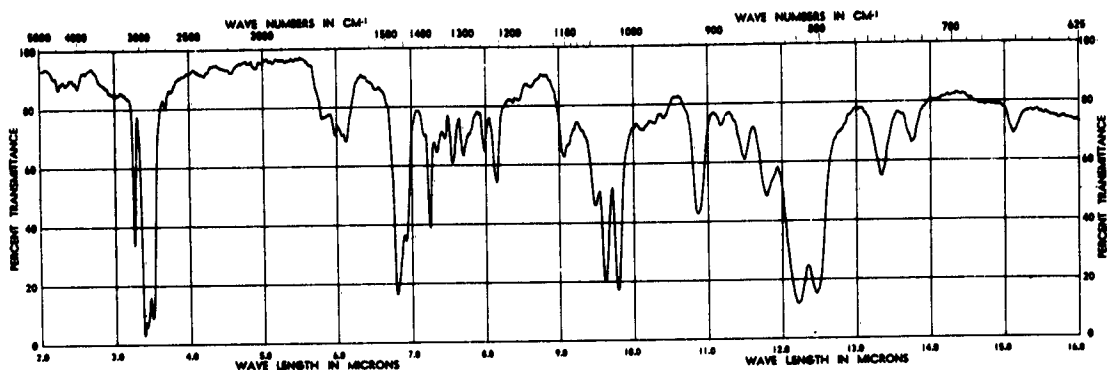


Figure 30. Infrared Spectrum of 1,1'-Dibutylferrocene (n_D^{20} 1.5485) in a 0.03 mm. Cell.

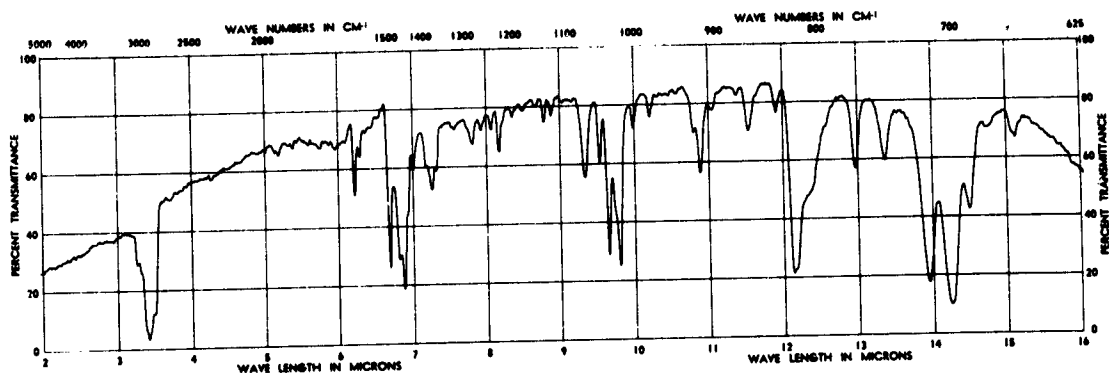


Figure 31. Infrared Spectrum of 1,1'-Dibenzylferrocene (M.P. 102-103°C) in Nujol Mull.

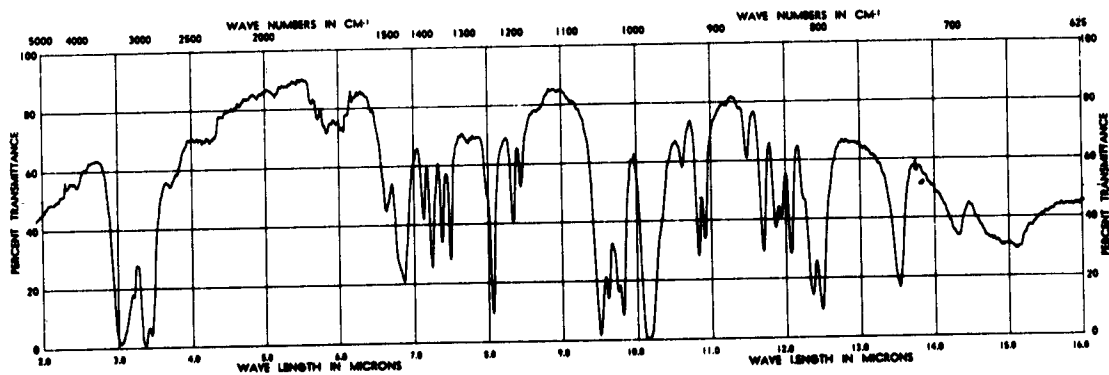


Figure 32. Infrared Spectrum of 1,1'-Di(hydroxymethyl)-ferrocene (M.P. 105-107°C) in Nujol Mull.

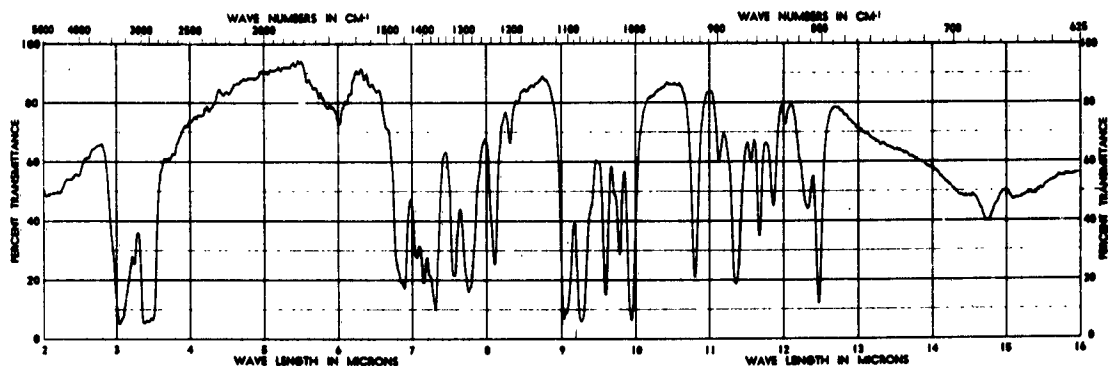


Figure 33. Infrared Spectrum of 1,1'-Bis(α -hydroxyethyl)-ferrocene (M.P. 69-71°C) in Nujol Mull.

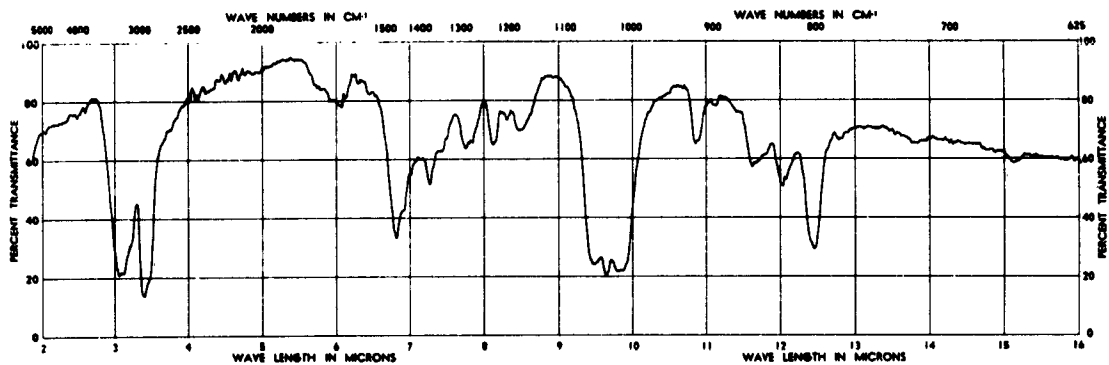


Figure 34. Infrared Spectrum of 1,1'-Bis(β -hydroxyethyl)-ferrocene (M.P. 43-45°C) in Nujol Mull.

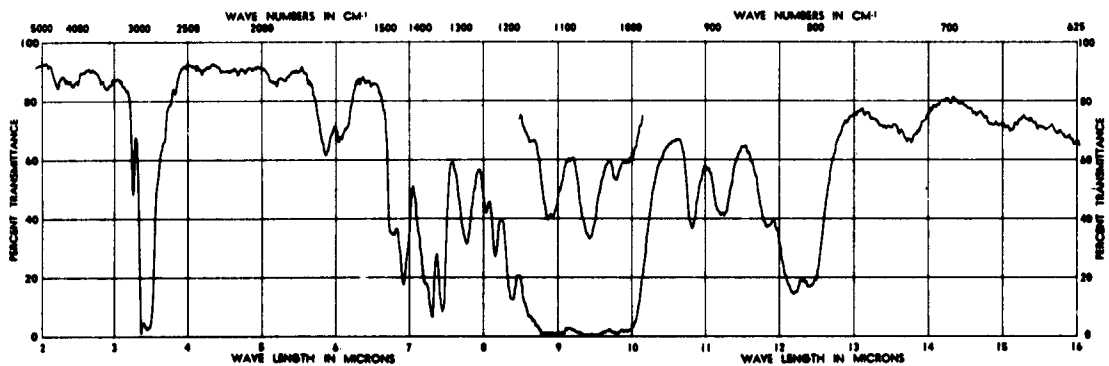


Figure 35. Infrared Spectrum of 1,1'-Bis(β,β -diethoxyethyl)-ferrocene (n_D^{25} 1.5096) in a Capillary.

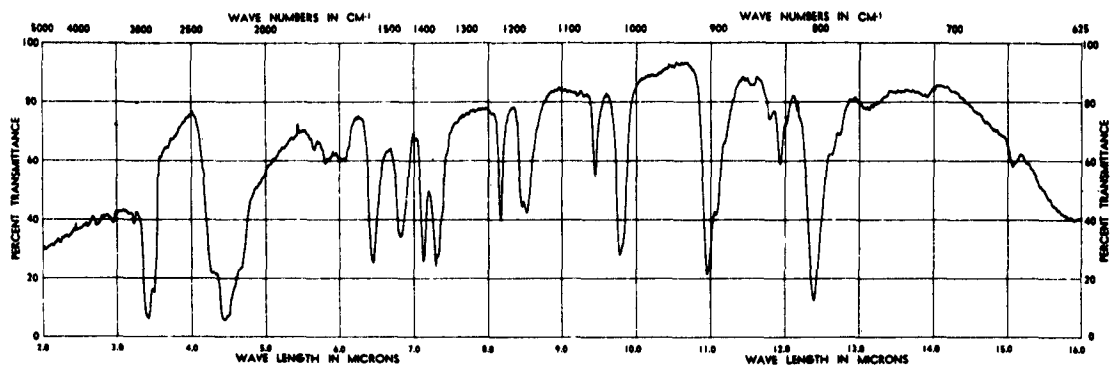


Figure 36. Infrared Spectrum of 1,1'-Ferrocene Diisocyanate (M.P. 81-82.5 and 86.5-87.5°C) in Nujol Mull.

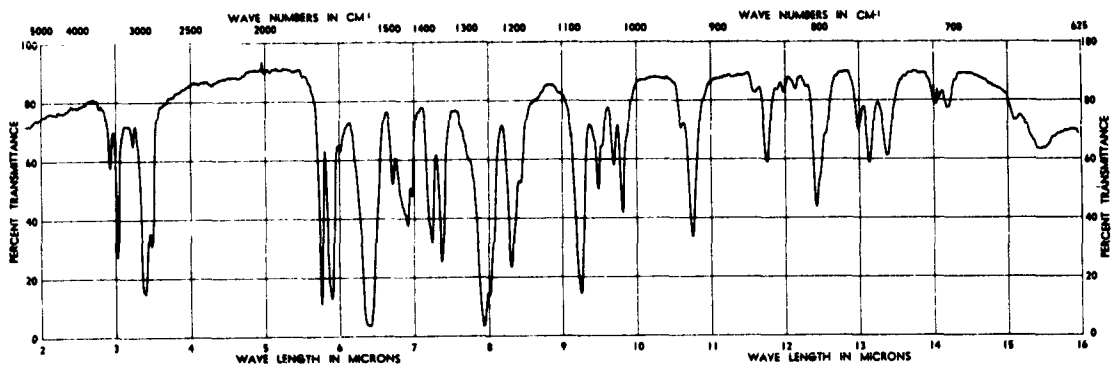


Figure 37. Infrared Spectrum of Dimethyl 1,1'-Ferrocenedicarbamate (M.P. 177-177.5°C) in Nujol Mull.

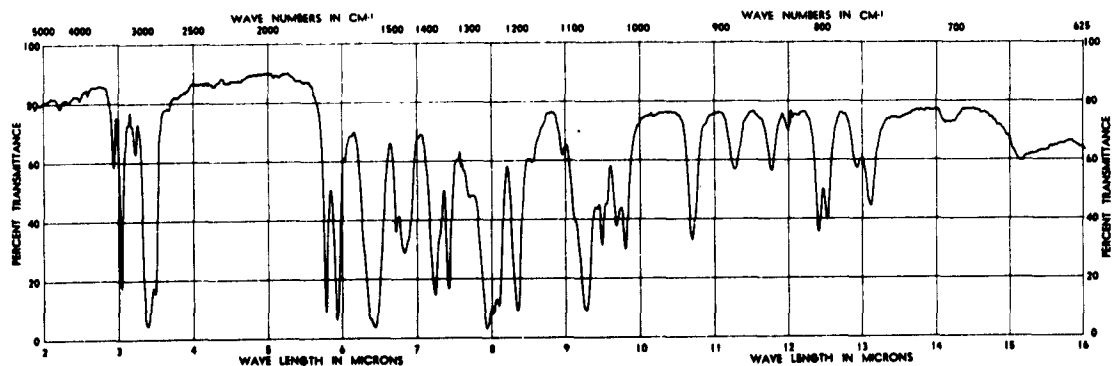


Figure 38. Infrared Spectrum of Diethyl 1,1'-Ferrocenedicarbamate (M.P. 119.5-120°C) in Nujol Mull.

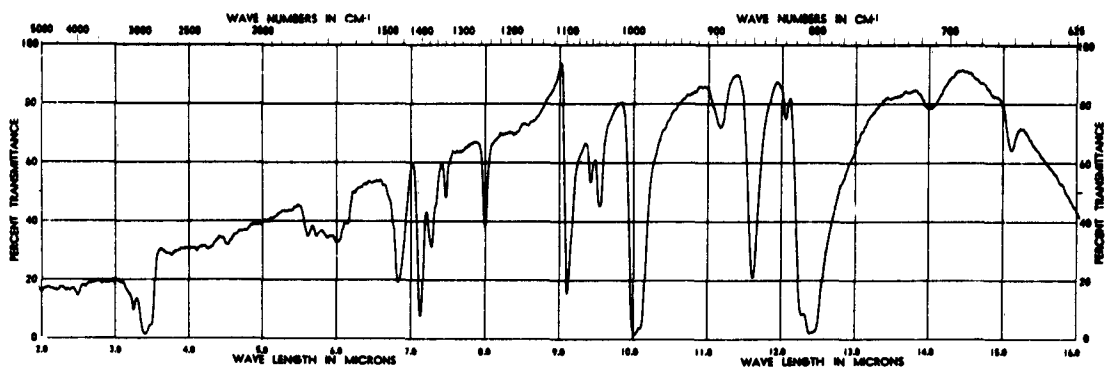


Figure 39. Infrared Spectrum of Ruthenocene (M.P. 197-200°C) in Nujol Mull.

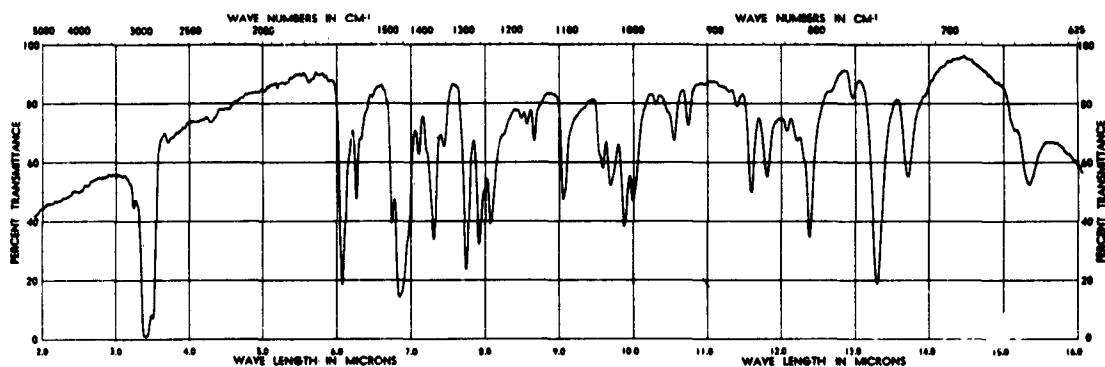


Figure 40. Infrared Spectrum of o-Methoxybenzoylruthenocene (M.P. 143-144°C) in Nujol Mull.

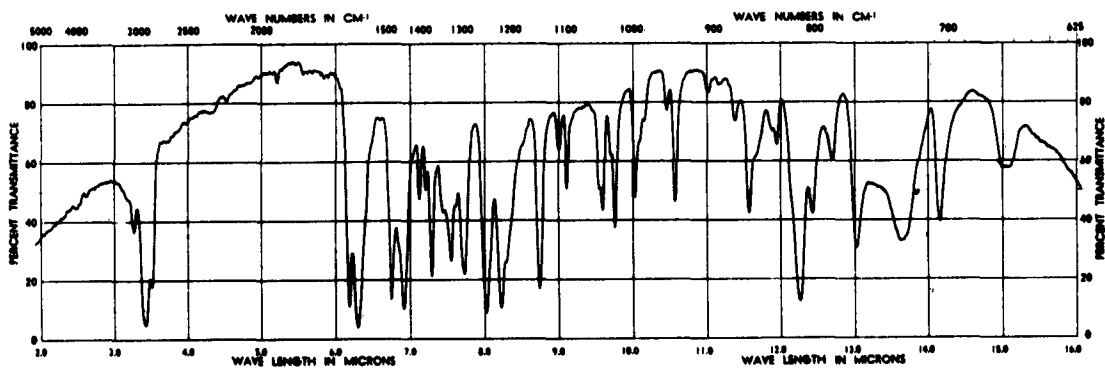


Figure 41. Infrared Spectrum of o-Hydroxybenzoylruthenocene (M.P. 92-93°C) in Nujol Mull.

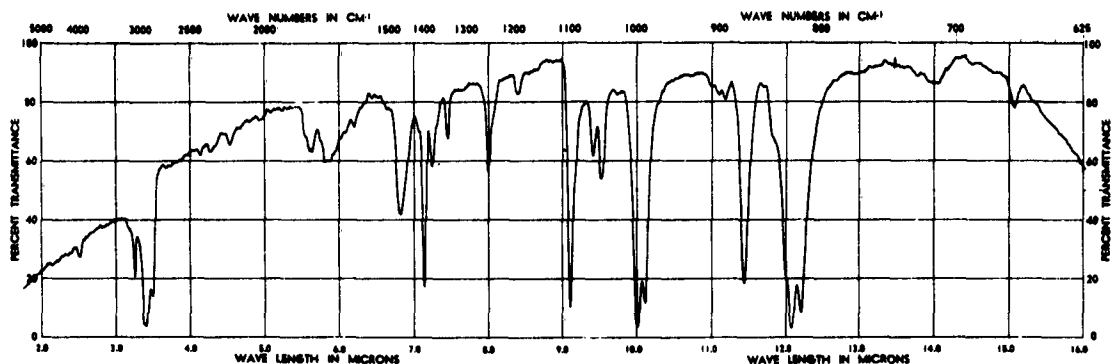


Figure 42. Infrared Spectrum of Osmocene (M.P. 226-227°C) in Nujol Mull.

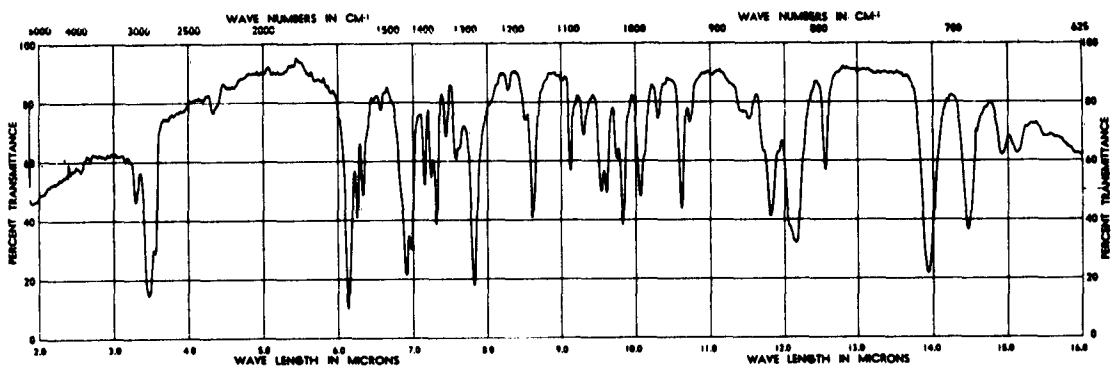


Figure 43. Infrared Spectrum of Benzoylosmocene (M.P. 131.5-132.5°C) in Nujol Mull.

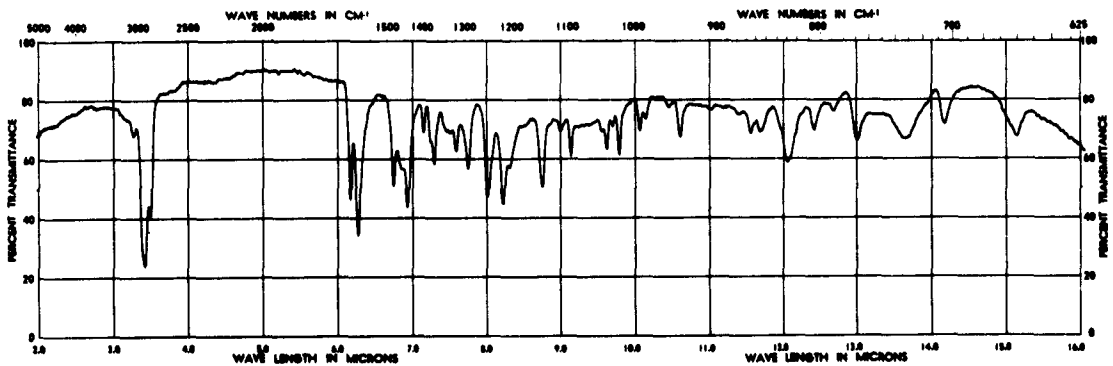


Figure 44. Infrared Spectrum of o-Hydroxybenzoylosmocene (M.P. 99-100°C) in Nujol Mull.

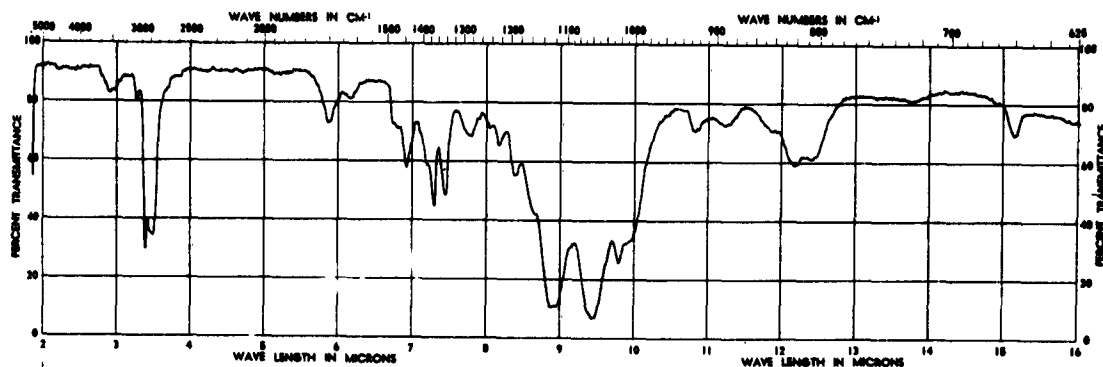


Figure 45. Infrared Spectrum of $[(\text{CH}_3\text{CH}_2\text{O})_2\text{CHCH}_2\text{C}_5\text{H}_4]_3\text{Hf}$ in a Capillary.

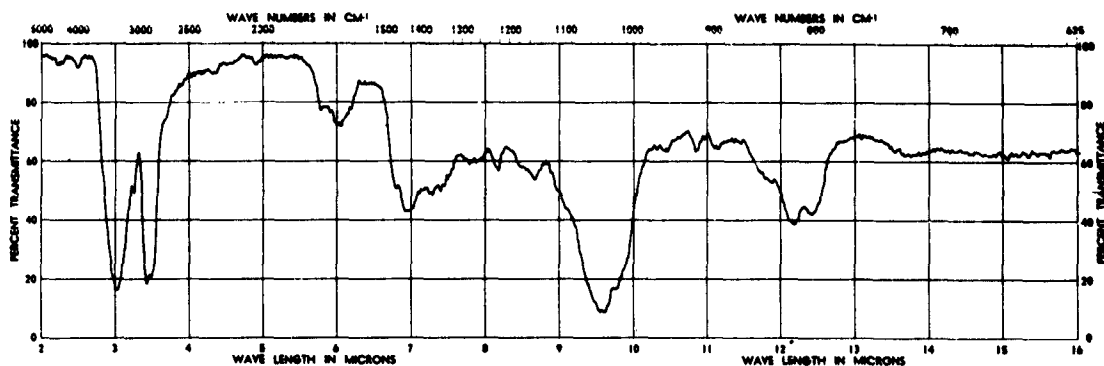


Figure 46. Infrared Spectrum of $(\text{HOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_4\text{H}_2\text{Fe}$ in a Capillary.

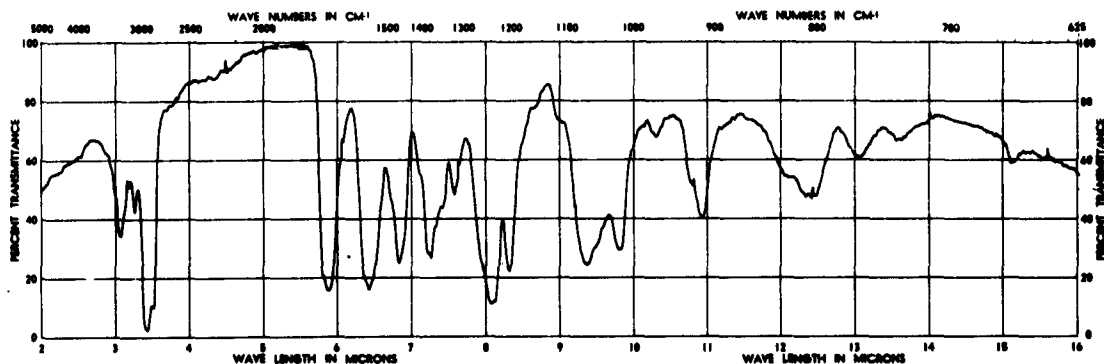


Figure 47. Infrared Spectrum of Soluble Poly(1,1'-ferrocenedimethyl 1,1'-ferrocenedicarboxylate) in Nujol Mtl.

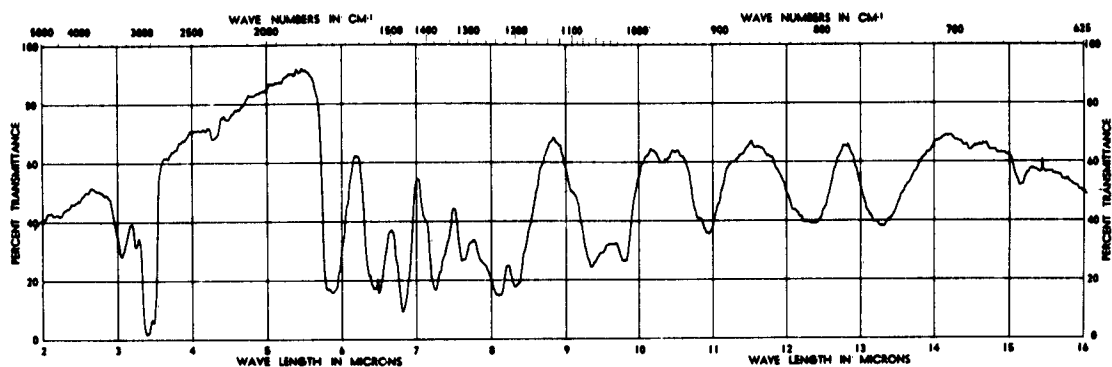


Figure 48. Infrared Spectrum of Insoluble Poly(1,1'-ferrocenedimethyl-1,1'-Ferrocenedicarbamate) in Nujol Mull.

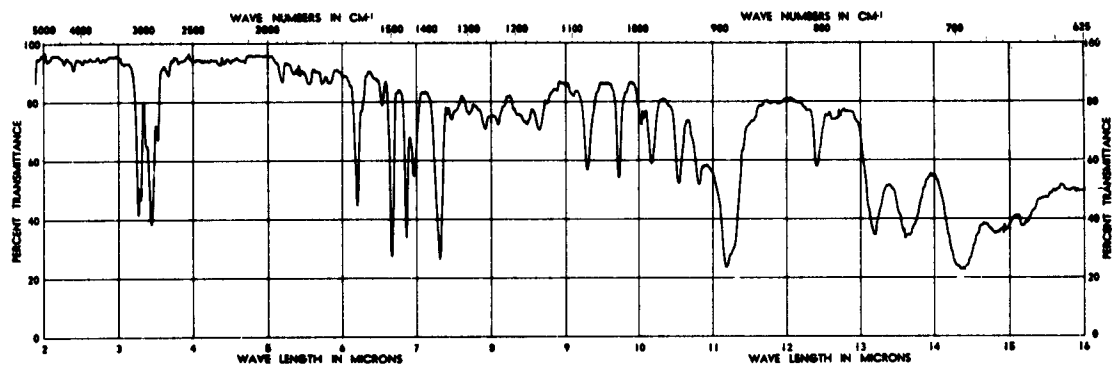


Figure 49. Infrared Spectrum of Crude Benzylcyclopentadiene in a 0.028 mm. Cell.

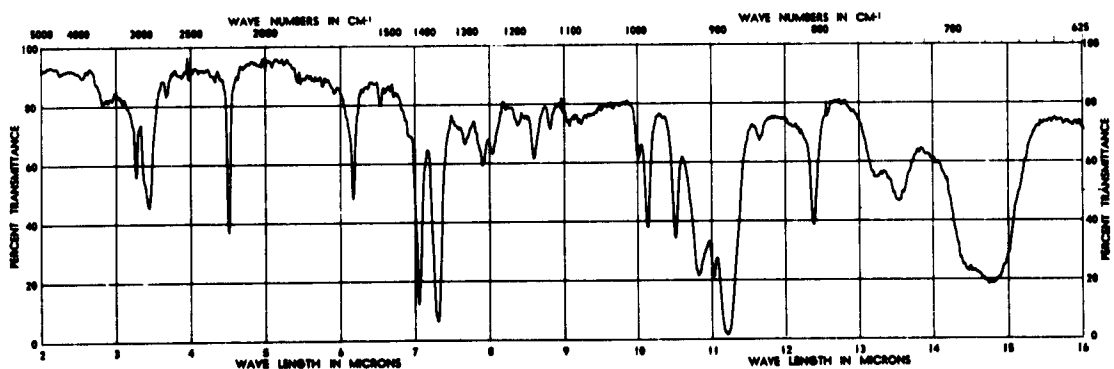


Figure 50. Infrared Spectrum of (Cyanomethyl)-cyclopentadiene (n_D^{20} 1.4581) in a 0.015 mm. Cell.

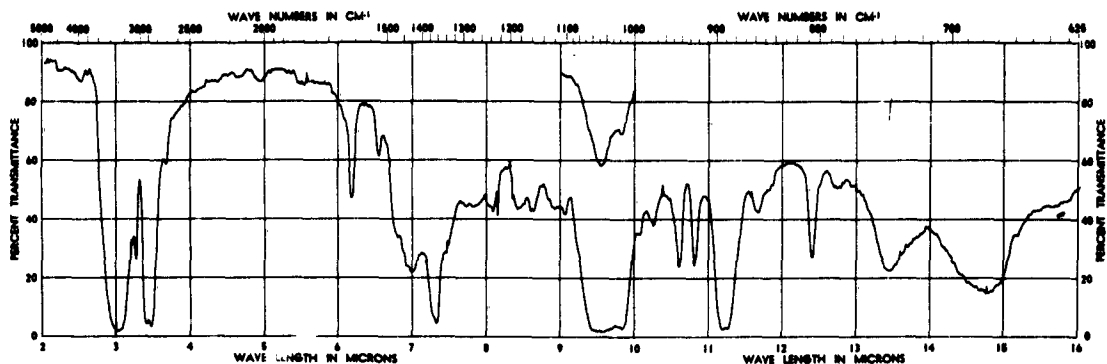


Figure 51. Infrared Spectrum of β -hydroxyethylcyclopentadiene (n_D^{25} 1.4917) in a 0.015 mm. Cell.

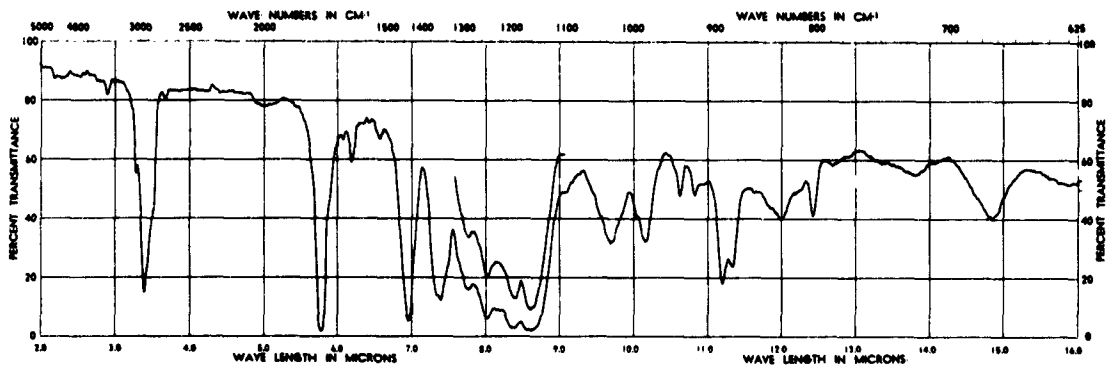


Figure 52. Infrared Spectrum of β -Carbomethoxyethylcyclopentadiene (n_D^{25} 1.4719) in a 0.02 mm. Cell and in a Capillary.

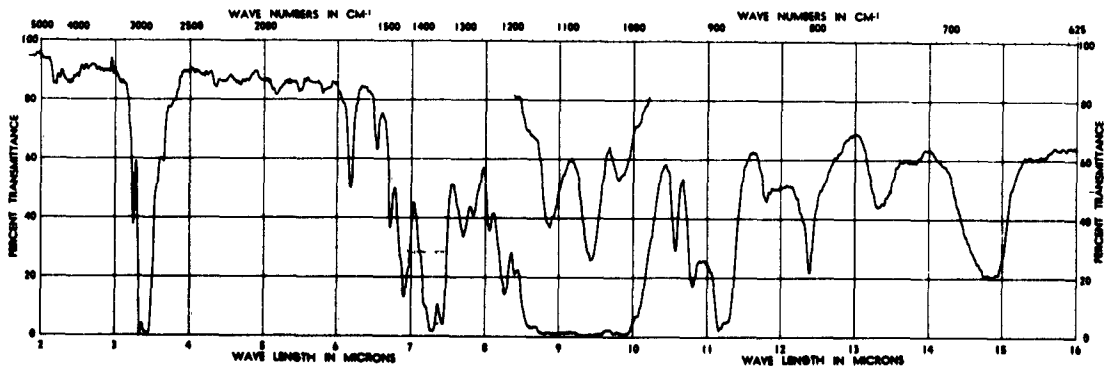


Figure 53. Infrared Spectrum of α,β -diethoxyethylcyclopentadiene (n_D^{25} 1.4548) in a 0.015 mm. Cell.

IV. SUMMARY AND CONCLUSIONS

A study of the preparation of difunctional ferrocenes from cyclopentadiene derivatives led to six new cyclopentadiene compounds, two dihydrofulvene derivatives, two new ferrocenes, and three organoiron compounds containing more than two substituted cyclopentadienes per iron atom. Urethanes prepared from 1,1'-ferrocenediisocyanate were no more thermally stable than other urethanes. From work on the preparation of osmocene and ruthenocene analogs of the hydroxybenzophenone class of ultraviolet absorbers, *o*-hydroxybenzoyl osmocene, *o*-methoxybenzoylruthenocene, and *o*-hydroxybenzoylruthenocene were prepared, and physical properties and spectral characteristics of these compounds and ruthenocene were determined. During this work, two new osmium oxychlorides were encountered.

Thus, the reaction of cyclopentadienylsodium or cyclopentadienyllithium with the following compounds gave the products noted: methyl 3-bromopropionate, 51% β -carbomethoxyethylcyclopentadiene and 15% bis(β -carbomethoxyethyl)-cyclopentadiene; chloroacetonitrile, 43% cyanomethylcyclopentadiene; chloroacetaldehyde diethyl acetal, 30% β,β -diethoxyethylcyclopentadiene and 35% 5,1-(α -diethoxymethyl- β -ethoxytrimethylene)-cyclopentadiene (assumed structure); ethylene oxide, 5% β -hydroxyethylcyclopentadiene and 14% bis(β -hydroxyethyl)-cyclopentadiene; ethyl chloroacetate, 29% 6-carbethoxy-3,4-dihydrofulvene and 12% carbethoxymethyl-6-carbethoxy-3,4-dihydrofulvene; benzyl chloride, 47% benzylcyclopentadiene; ethylene dichloride, 22% crude vinylcyclopentadiene and a crude hydrocarbon, $C_{14}H_{18}$, ca. Structures of these products were established primarily by elemental analyses and examination of ultraviolet spectra. Strong absorption in the infrared at 11 to 11.3 readily differentiated the cyclopentadiene compounds from the corresponding dimers, which absorbed weakly, at most, in this region.

Four of the cyclopentadiene compounds could be converted to ferrocenes. Thus, treatment of β,β -diethoxyethylcyclopentadiene with isopropylmagnesium chloride and ferrous chloride furnished 13-39% 1,1'-bis(β,β -diethoxyethyl)-ferrocene, 2% β,β -diethoxyethylcyclopentadienyliron bis(β,β -diethoxyethyl)-cyclopentadiene), and returned 24-27% of the acetal. Similarly, 5,1-(α -diethoxymethyl- β -ethoxytrimethylene)-cyclopentadiene gave the crude ferrocene and 3% $(C_{15}H_{23}O_3)_4H_2Fe$. From β -hydroxyethylcyclopentadiene with butyllithium and ferrous chloride was isolated 19% 1,1'-bis(β -hydroxyethyl)-ferrocene, 13% bis(β -hydroxyethylcyclopentadienyl)-iron bis(β -hydroxyethylcyclopentadiene), and 14% starting cyclopentadiene compound. Benzylcyclopentadiene was converted to 1,1'-dibenzylferrocene (45-72%) with methyllithium and ferrous chloride. Attempts were made to convert butadiene, allyl chloride, or cyclopentadiene to iron compounds analogous to the structures tentatively assigned to the by-products from these sandwiching reactions, but the yields or iron-containing products were very low.

Urethanes prepared from 1,1'-ferrocene diisocyanate and methanol, ethanol, and 1,1'-di(hydroxymethyl)-ferrocene decomposed in the range 245-280°C. The diol yielded both a soluble and an insoluble polyurethane. Hydrolysis of the diisocyanate gave 61% poly(ferrocenyleneurea) (or the bridged urea; the structure was uncertain).

An attempted Friedel-Crafts reaction on ferrocene with chloroacetaldehyde diethyl acetal resulted primarily in oxidation of the ferrocene and ferrocenyl-products. Reactions of acetaldehyde and epichlorohydrin on lithiated ferrocene returned 57% and 83% ferrocene, respectively, while benzaldehyde gave oils contaminated with butylphenylcarbinol. From reduction of chloroacetylferrocene with sodium borohydride, alcohols were obtained but not in pure form.

Osmocene with excess *o*-methoxybenzoylchloride and aluminum chloride furnished about 45% crude *o*-methoxybenzoylosmocene and returned 47% osmocene. When solvent was removed from a similar reaction mixture and the residue heated at 90°C, 25% *o*-hydroxybenzoylosmocene was isolated and 31% osmocene recovered. For use in preparation of the starting osmocene, osmium tetrachloride was prepared by a known method in 85% yield by chlorination of osmium at 700°C. When the chlorination was conducted with a 15 to 1 mixture of chlorine and air, diosmium oxide octachloride was obtained in 77% yield along with 10% tetrachloride. The oxychloride decomposed to osmium trichloride at 125°C/5 mm. A commercial "anhydrous osmium trichloride" when heated at 500°C left another oxychloride, $(Os_2Cl_3O_2)_n$.

o-Hydroxybenzoylruthenocene was prepared from ruthenocene by treatment with one equivalent each of *o*-methoxybenzoyl chloride and aluminum chloride, finally at 90°C. In addition to the *o*-hydroxy compound (33% yield, crude), the *o*-methoxy compound was also isolated (29%). Treatment of bis(cyclopentadienyl)-magnesium in toluene with ruthenium trichloride gave 6% ruthenocene.

The ruthenocene and osmocene compounds absorbed considerably less in the visible region than the corresponding ferrocene analogs.

Some experimental work was conducted after the bulk of this report was written. Thus, a procedure reported by Rausch, *et al.* (22), to give primarily benzoylruthenocene and a little dibenzoylruthenocene was repeated with one-fourth the stated amount of solvent and twice the reaction time, and it yielded exclusively dibenzoylruthenocene, according to infrared analysis (77%, m.p. 124-5°C, and 13% of very crude material). A repeat preparation of *o*-hydroxybenzoylruthenocene gave 64% *o*-hydroxy compound, m.p. 88.5-92°C, and 21% *o*-methoxybenzoylruthenocene, m.p. 143.5-144.5°C. A third preparation of ruthenocene gave a 29% yield of material m.p. 197-200°C.

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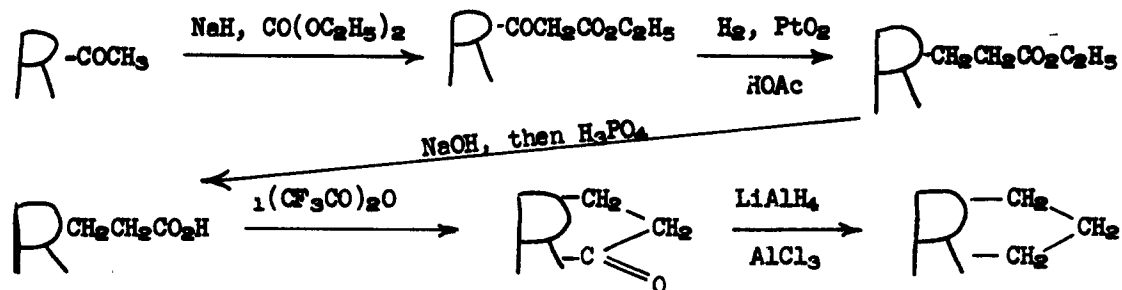
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I. DISCUSSION

I. DISCUSSION

The general route employed in the present study for the introduction of trimethylene bridges was that described earlier (2) for the preparation of I: carbethoxylation of the acetyl compound with diethyl carbonate, employing a dispersion of sodium hydride in mineral oil suspended in a hydrocarbon solvent; hydrogenolysis of the resulting β -keto ester over platinum oxide in acetic acid, saponification of the propionate ester; cyclization of the propionic acid with trifluoroacetic anhydride in carbon tetrachloride; reduction of the bridged ketone to the hydrocarbon with lithium aluminum hydride-aluminum chloride.



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by the trimethylene bridge at the 2'-position of the second ring, since homoannular cyclization was not observed in the cyclization of the unsubstituted ferrocene propionic acid (2) or of the bridged-3-propionic acid (IX).

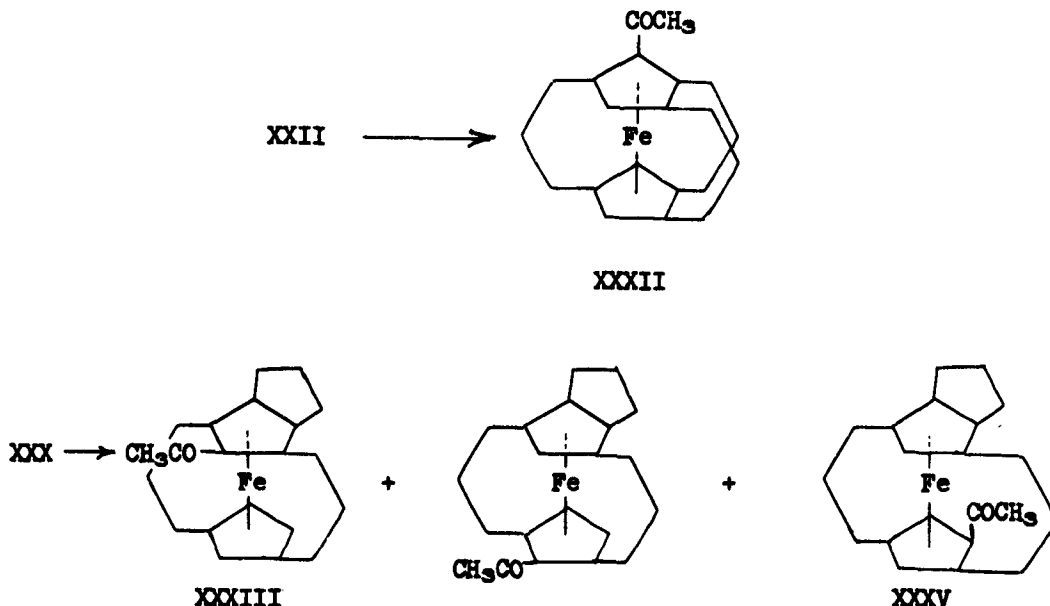
An alternative route to VI and X in the present study was employed earlier by Schlögl and Seiler (3) from 1,1'-ferrocenedipropionic acid (XII). Although the earlier authors reported only one isomer (X) from this reaction sequence, we have isolated both VI and X, identical to the compounds obtained from the 2-acetyl- and 3-acetyl-1,1'-trimethyleneferrocenes, II and III, respectively. The failure of Schlögl and Seiler to observe both isomers could lie in some purification step, since in the present work no attempt was made to purify the intermediates between the dipropionic acid (XII) and the keto-dibridged compounds (VI and X). In contrast to the results of the route from II, no homoannularly cyclized product (VIII) was isolated in the route from XII. This is not surprising since only a small amount of VI (1% vs. 32% of X) was found and the amount of VII would be only about one-fourth that of VI.

From the α -dibridged VIII it was possible to prepare both isomeric tribridged compounds 1,1'; 2,2'; 3,3'- and 1,1'; 2,2'; 4,4'-tris-(trimethylene)ferrocenes, XVIII and XXII, respectively, employing the general procedures described above (Fig. 2). The first step involved acetylation of VIII to give 3-acetyl- and 4-acetyl-1,1',-2,2'-bis-(trimethylene)ferrocenes XIII and XIV, respectively. The infrared spectra of the isomers were of less direct help in establishing their structures in this case, since trisubstituted ferrocenyl rings have not previously been investigated. Other evidence for the structures were the longer wave length but lower extinction coefficient of the 4-acetyl isomer's maximum near 225 m μ , the prior elution from alumina of the 3-acetyl isomer and, conclusively, the n.m.r. spectra of the two compounds which are discussed below. The overall yield of XVIII from XIII was 8%, that of XXII from XIV was 47%. Here again, in the isomeric pair of propionic acids XV and XX, the less hindered propionic acid XX gave only heteroannular cyclization, while the more hindered XV gave a mixture of heteroannularly and homoannularly cyclized ketones, XVI and XVII, respectively. In this case, homoannular cyclization predominated (9% yield of XVI from XIII, 19% yield of XVII). The structures of the two cyclization products were established by their n.m.r. and their ultraviolet spectra.

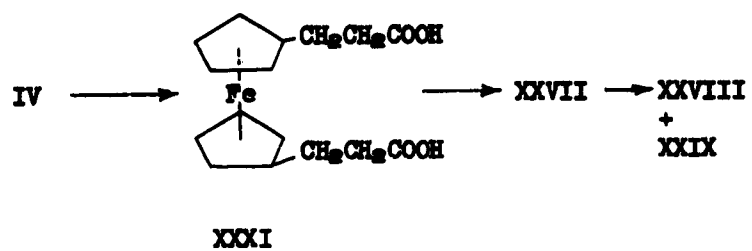
From the β -dibridged XI it was possible to prepare the 1,2,4-tribridged XXII (Fig. 3), as described in the previous report (1). 4-Acetyl-1,1',3,3'-bis-(trimethylene)ferrocene (XXIV), together with its 2-acetyl isomer (XXIII), was obtained by acetylation of the β -dibridged compound XI, as described before (1). Attempts to cyclize the propionic acid XXV, obtained from XXIII, with trifluoroacetic anhydride gave only a compound tentatively identified as the trifluoromethyl ketone XXVI, and unchanged acid. Trifluoromethyl ketone formation was observed earlier as a side reaction in the preparation of 1,1'- α -ketotrimethyleneferrocene (I) from β -ferrocenylpropionic acid (2); here, probably due to steric resistance to closure between the two trimethylene

bridges, it is the sole reaction. An attempt to cyclize the propionic acid XXV in polyphosphoric acid gave tar and the Friedel-Crafts reaction of its acid chloride gave only recovered starting material.

Cyclization of XXVII gave, in addition to XXVIII, the homoannular ketone XXIX. Each of these was reduced to the hydrocarbon - XXII from XXVIII, XXX from XXIX. The n.m.r. spectra of XXII and XXX are conclusive in establishing their structures, and additional evidence in distinguishing between them is provided by their acetylation products. The tribridged compound (XXII) is quite symmetrical and would be expected to give only one mono-acetylation product, which it does (in 82% yield). On the other hand, compound XXX should give three isomeric mono-acetylation products. Acetylation of XXX did, indeed, give a mixture of mono-acetyl derivatives and evidence was obtained for the presence of at least three of these. One of them, 4'-acetyl-1,1';2,2';4,5-tris-(trimethylene)ferrocene (XXXV) was obtained in pure form, but the other two isomers could not be separated on alumina. However, the n.m.r. spectrum of the mixture establishes the presence of the two isomers (XXXIII and XXXIV).



The disubstituted third product from acetylation of 1,1'-trimethyleneferrocene (I), 3,4'-diacetyl-1,1'-trimethyleneferrocene (IV), was converted to the dipropionic acid XXXI which, when subjected to the series of reactions employed for ferrocene-dipropionic acid, gave the same heteroannular and homoannular ketones (XXVIII and XXIX, respectively) obtained from cyclization of XXVII.



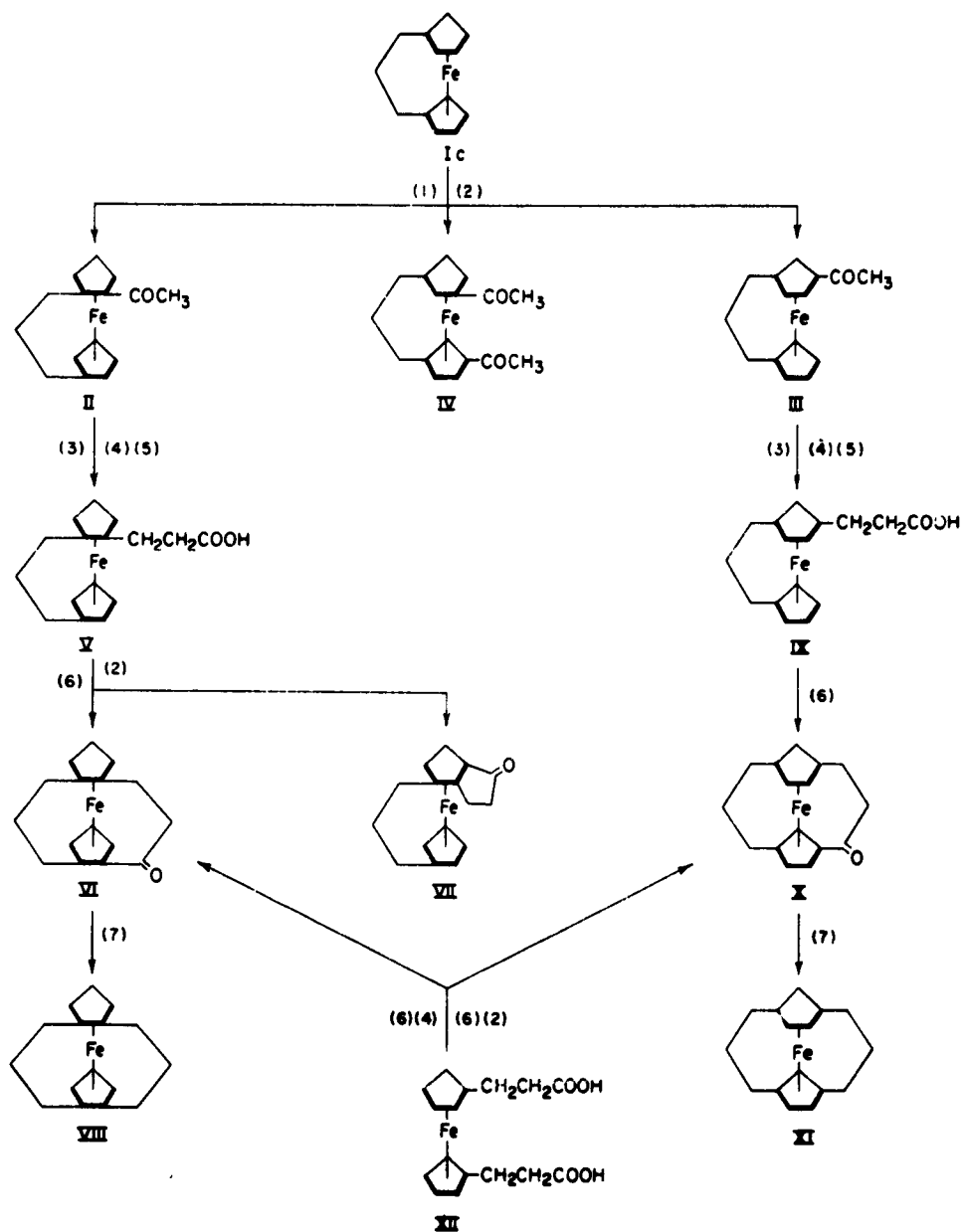


Figure 1 Synthetic Routes to 1,1',2,2'- and 1,1',3,3'-bis-(trimethylene)ferrocene (VIII and XI). Numbered Steps: (1) $(\text{CH}_3\text{CO})_2\text{O}$, AlCl_3 ; (2) Chromatographic Separation; (3) NaH , $\text{CO}(\text{OC}_2\text{H}_5)_2$; (4) H_2 , PtO_2 , CH_3COOH ; (5) NaOH , then H_3PO_4 ; (6) $(\text{CF}_3\text{CO})_2\text{O}$; (7) LiAlH_4 - AlCl_3 .

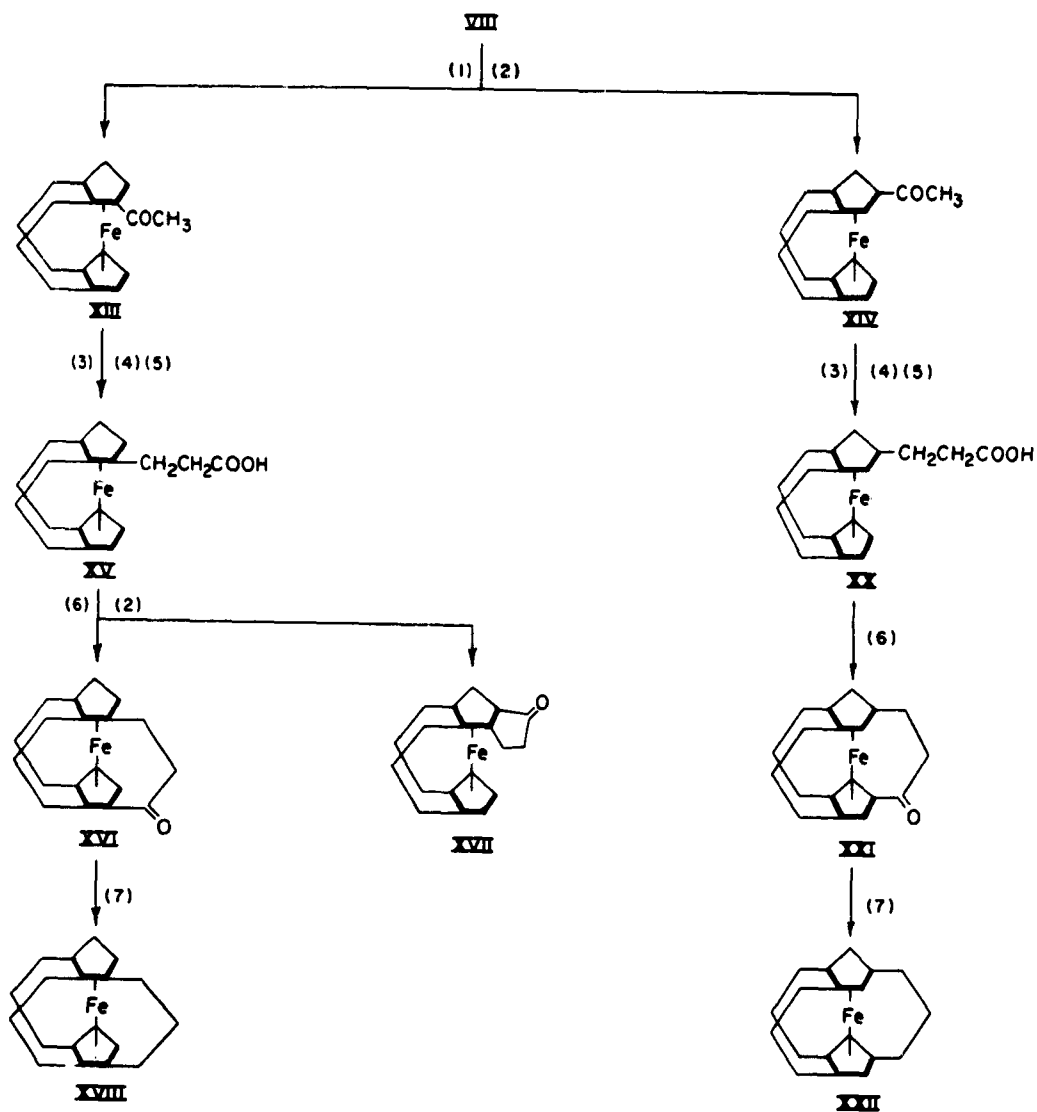


Figure 2 Products from 1,1',2,2'-bis-(trimethylene)-ferrocene (VIII). Numbered Steps Same as in Figure 1.

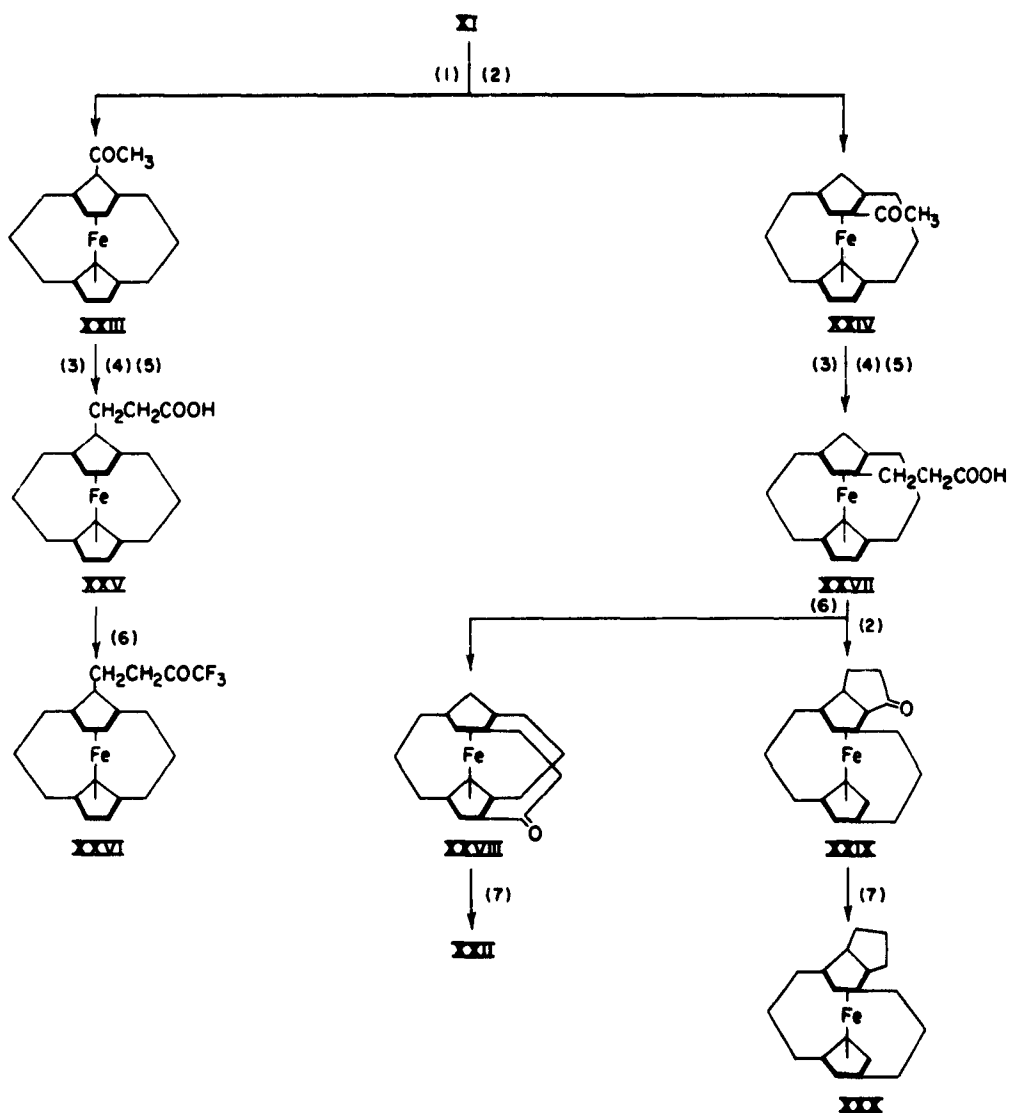


Figure 3 Products from 1,1',3,3'-bis-(trimethylene)ferrocene (XI).
Numbered Steps Same as in Figure 1.

II. EXPERIMENTAL

Conversion of 2-acetyl-1,1'-trimethyleneferrocene (II) to 1,1',2,2'-bis-(trimethylene)-ferrocene (VIII) was effected via the method employed earlier (1) for the conversion of acetylferrocene to 1,1'-trimethyleneferrocene. A solution of 1.0 g. (3.25 mmoles) of II in 150 ml. of xylene was added dropwise, under nitrogen, to a stirred mixture of 0.32 g. (6.6 mmoles) of a mineral oil dispersion of sodium hydride (50%) and 0.78 g. (6.6 mmoles) of diethyl carbonate in 225 ml. of xylene. Reflux was maintained during addition and for 12 hours thereafter, when the mixture was cooled to room temperature and hydrolyzed with ice water containing 10 mmoles of hydrochloric acid. After separation from the aqueous phase, the organic layer was dried over magnesium sulfate. Evaporation of the solvent left the β -keto ester as a viscous red oil.

The crude β -keto ester was dissolved in 40 ml. of acetic acid and hydrogenolyzed over 1.0 g. of platinum oxide at 40 p.s.i. for 46 hours, at which time hydrogen uptake had ceased. The solution was filtered and acetic acid was removed on a rotary evaporator. A solution of the residual ester (crude 1.1 g. 90 percent), in 50 ml. of ethanol and 4.0 ml. of 2N sodium hydroxide was heated for 2 hours at reflux. The basic solution was diluted with water and washed repeatedly with ether, then acidified with phosphoric acid, and extracted with ether. The acidic ether extract was dried over magnesium sulfate and evaporated to dryness to give 0.9 g. (crude, 89 percent) of the propionic acid V.

A solution of the propionic acid in 200 ml. of carbon tetrachloride, which has been previously bubbled with nitrogen, and 4.0 g. of trifluoroacetic anhydride was stirred for 4 hours in a dark, stoppered flask, then poured into an excess of sodium bicarbonate solution. The aqueous layer was extracted with methylene chloride and the organic extract was dried over magnesium sulfate, then evaporated to dryness. The residue, in a minimal amount of benzene, was placed on an alumina column (Alcoa F-20, activity III, 1.8 cm. x 60 cm.). Elution with 2% ether in Skelly B gave 0.206 g. (19% from II) of 2,2'-(α -ketotrimethylene)-1,1'-trimethyleneferrocene (VI), whose structure was assigned from its spectral properties. Recrystallization from Skelly B gave 0.16 g. of red-brown crystals which underwent a form modification at 199-201° and decomposed above 220°.

Anal. Calc'd. for $C_{16}H_{16}FeO$: C, 68.59; Fe, 19.95; Mol. wt. 280.
Found: C, 68.75; H, 5.82; Fe, 19.76; Mol. wt. (Osmometer), 296.

Elution of the same column with 20% ether in Skelly B gave 0.053 g. (5%) of the homoannular ketone 3,2-(α -ketotrimethylene)-1,1'-trimethyleneferrocene (VII), m.p. 132.0-133.0°, also identified by its spectral properties.

Anal. Found: C, 68.25; H, 5.73; Fe, 19.77; Mol. wt. (Osmometer), 269.

A solution of 0.53 g. (1.9 mmol) of the above 2,2'-(α -ketotrimethylene)-1,1'-trimethyleneferrocene (VI) in 100 ml. of ether was added dropwise to a stirred mixture of 0.30 g. (2.3 mmol) of aluminum chloride and 0.087 g. (2.3 mmol) of lithium aluminum hydride in 100 ml. of ether. Reflux was maintained during addition and for 30 minutes thereafter. The reaction was cooled in an ice bath and carefully decomposed with wet ether. Water was added, the layers were separated, and the organic layer was dried over magnesium sulfate, filtered, and evaporated to 0.462 g. (91%) of 1,1'-2,2'-bis-(trimethylene)ferrocene. Recrystallization from hexane gave 0.45 g. of yellow crystals, m.p. 216-218°, after a crystal modification at 191-192°. The material sublimed at 120°/0.05 mm. The nuclear magnetic resonance spectrum is presented in Table V.

Anal. Calc'd. for $C_{18}H_{18}Fe$: C, 72.20; H, 6.82; Fe, 20.99.
Found: C, 73.14; H, 7.51; Fe, 19.03.

Conversion of 3-acetyl-1,1'-trimethyleneferrocene (III) to 1,1',3,3'-bis-(trimethylene)ferrocene (XI) followed precisely the procedure described above for the 2-acetyl isomer. From 10.0 g. (37 mmol) of III, 3.5 g. (73 mmol) of a mineral oil dispersion of sodium hydride (50%) and 8.8 g. (75 mmol) of diethyl carbonate in a total of 75 ml. of benzene was obtained 12.2 g. (96%) of crude β -keto ester. From this β -keto ester was obtained, after hydrogenolysis (over 1.0 g. of platinum oxide at 40 p.s.i.) and saponification, 6.7 g. (61%) of crude propionic acid IX. From the propionic acid (6.7 g., 22 mmol) and 25 ml. of trifluoroacetic anhydride in 200 ml. of carbon tetrachloride was obtained, after work-up and chromatography (10% ether in Skelly B elutant), 6.3 g. (60% from III) of 3,3'-(α -ketotrimethylene)-1,1'-trimethyleneferrocene (X), m.p. 107-110° (lit.¹³ 110-113°). No isomeric ketone was obtained from the chromatography.

Anal. Calc'd. for $C_{18}H_{18}FeO$: C, 68.59; H, 5.76; Fe, 19.95; Mol. wt., 280.
Found: C, 69.01; H, 5.83; Fe, 19.52, Mol. wt. (Osmometer) 280.

As in the preceding section, the ketone X, (0.73 g., 2.6 mmol) was converted by lithium aluminum hydride (0.99 g., 26 mmol)-aluminum chloride (5.2 g., 39 mmol) reduction to the hydrocarbon bridged compound, 1,1',3,3'-bis-(trimethylene)ferrocene (XI, 0.69 g. quantitative), which melted 89.0-91.5° (lit.¹³ 88-91°) after recrystallization from hexane. Nuclear magnetic resonance spectral data are presented in Table V.

Cyclization Products from 1,1'-Ferrocenedipropionic Acid (XII). A mixture of 4.8 g. (14.5 mmol) of 1,1'-ferrocenedipropionic acid, 250 ml. of deoxygenated carbon tetrachloride and 24 g. (114 mmol) of trifluoroacetic anhydride was stirred for 4 hours under nitrogen in the dark at room temperature, then poured into excess sodium bicarbonate solution. The aqueous layer was extracted with methylene chloride and the combined organic layers were washed with water, dried and concentrated to a viscous red-brown oil, the crude keto-bridged propionic acid mixture (4.5 g., 98%). This material, in acetic acid,

was hydrogenolyzed for 24 hours over 1.0 g. of platinum oxide at room temperature and 40 p.s.i. The mixture was filtered and poured into water, and the resulting suspension was extracted with ether. The ether extract was washed to neutrality with water, then dried and concentrated to a yellow-brown oil, the crude mixed propionic acids V and IX (3.9 g., 86%).

The mixture was cyclized under the precise conditions employed in the preceding paragraph for the cyclization of the dipropionic acid (XII). The neutral product from the cyclization was chromatographed over alumina (Alcoa F-20, activity III, 1.8 cm. x 50 cm.). Elution with 2% ether in Skelly B removed 0.10 g. (1%) of 2,2'-(α -ketotrimethylene)-1,1'-trimethyleneferrocene (VI) whose spectral properties and melting behavior were identical with those of the same compound obtained from II. After the compound had been recrystallized from Skelly B it underwent a crystal modification at 198-199° and decomposed above 225°.

Anal. Found: C, 68.73; H, 5.82; Fe, 19.50; Mol. wt. (Osmometer), 262.

Elution with 20% ether in Skelly B removed 0.99 g. (43%) of 3,3'-(α -ketotrimethylene)-1,1'-trimethyleneferrocene (X), m.p. 111.0-112.3° (lit.¹³ 110-113), whose infrared spectrum was identical to that of the compound above from III. In other runs the yields of mixed keto-bridged propionic acids, hydrocarbon bridged propionic acids, and dibridged products were 98%, 56%, and 33%, respectively.

Acetylation of 1,1',2,2'-bis-(Trimethylene)ferrocene (VIII). A mixture of 0.40 g. (3.0 mmoles) of aluminum chloride and 0.32 g. (3.1 mmoles) of acetic anhydride in 25 ml. of methylene chloride was added dropwise under nitrogen to a stirred, refluxing solution of 0.75 g. (2.7 mmoles) of 1,1',2,2'-bis-(trimethylene)-ferrocene in 25 ml. of methylene chloride. The solution was heated for 8 hours under reflux, then worked up in the usual manner and the reaction product was chromatographed over alumina. Elution with Skelly B gave 0.162 g. (22%) of unchanged 1,1',2,2'-bis-(trimethylene)-ferrocene, while elution with 5% ether in Skelly B gave 0.339 g. (41%) of 3-acetyl-1,1',2,2'-bis(trimethylene)ferrocene, (XIII), identified by its infrared, ultraviolet and n.m.r. spectra. Recrystallization from Skelly B gave 0.34 g. of red needles, m.p. 162.0-163.5°.

Anal. Calc'd. for $C_{18}H_{20}FeO$: C, 70.14; H, 6.54; Found: C, 69.99; H, 6.66.

Elution with 20% ether in Skelly B removed 0.24 g. (30%) of 4-acetyl-1,1'-2,2'-bis-(trimethylene)ferrocene, (XIII), identified by its infrared, ultraviolet and n.m.r. spectra. The compound was recrystallized from hexane and had m.p. 126.0-127.5°.

Anal. Found: C, 69.83; H, 6.57.

In another reaction 38% of the 3-acetyl isomer XIII, 25% of the 4-acetyl isomer XIV, and 25% of unchanged hydrocarbon were obtained. Thus, the ratio of 3-acetyl to 4-acetyl isomer in the two runs was 1.45 ± 0.08 to 1.00.

Conversion of 3-acetyl-1,1',2,2'-bis-(trimethylene)ferrocene (XIII) to 1,1',2,2',3,3'-tris-(trimethylene)ferrocene (XVIII) followed the conversion of II to VIII. The mixture of 0.52 g. (1.7 mmoles) of XIII, 3.8 mmoles of sodium hydride and 0.48 g. (3.2 mmoles) of diethylcarbonate in 60 ml. of xylene was heated at reflux for 16 hours after addition, then worked up as usual to give the β -keto ester. The latter was hydrogenolyzed over 0.5 g. of platinum oxide at 40 p.s.i. Isolation of the reduced ester and saponification in refluxing ethanolic sodium hydroxide then followed to give, after acidification, the crude propionic acid XV.

A solution of the crude acid, 50 ml. of carbon tetrachloride and 2 ml. of trifluoroacetic anhydride was stirred in the dark for 4 hours, then worked up in the usual manner. Chromatography of the neutral material over alumina (activity grade III) with 2% ether in Skelly B as elutant removed 0.045 g. (9% from acetyl compound) of 3,3'-(α -ketotrimethylene)-1,1',2,2'-bis-(trimethylene)ferrocene, (XVI), identified by its infrared, ultraviolet, and nuclear magnetic resonance spectra. Recrystallization from Skelly B gave 0.04 g. of yellow crystals, m.p. 190-193°, after a crystalline modification at 183-187°.

Continued elution with 20% ether in Skelly B, removed 0.102 g. (19% from acetyl starting material) of 4,3-(α -ketotrimethylene)-1,1',2,2'-bis-(trimethylene)ferrocene (XVII), identified by its nuclear magnetic resonance, infrared, and ultraviolet spectra. Recrystallization from hexane-benzene gave red-brown crystals, m.p. 160-163°.

Anal. Calc'd. for $C_{18}H_{20}FeO$: C, 71.31; H, 6.30; Fe, 17.45.
Found: C, 70.85; H, 6.22; Fe, 17.64.

Reduction of 30 mg. of the ketone XVI with a 10-fold excess of lithium aluminum hydride - aluminum chloride gave 28.6 mg. (92%) of 1,1',2,2',3,3'-tris-(trimethylene)ferrocene (XVIII). Sublimation at 130°/0.08 mm. gave a yellow solid, m.p. 178-181°, after a crystalline modification at 138-148°.

Anal. Calc'd. for $C_{18}H_{22}Fe$: C, 74.52; H, 7.24; Fe, 18.24.
Found: C, 74.05; H, 7.37; Fe, 17.77.

Conversion of 4-acetyl-1,1',2,2'-bis-(trimethylene)ferrocene (XIV) to 1,1',2,2',4,4'-tris-(trimethylene)ferrocene (XXII) followed the conversion of II to VIII. The mixture of 0.356 g. (1.14 mmoles) of XIV, 2.20 mmoles of sodium hydride and 0.28 g. (2.37 mmoles) of diethyl carbonate in 40 ml. of xylene was heated at reflux for 18 hours after addition, then worked up in the

usual manner. The crude β -keto ester was hydrogenolyzed over 0.5 g. of platinum oxide at 40 p.s.i., and the reduced ester then saponified to give 0.50 g. of the crude propionic acid XX.

A mixture of the acid, 20 ml. of carbon tetrachloride and 2 ml. of trifluoroacetic anhydride was stirred in the dark for 4 hours, then worked up as usual. Chromatography of the neutral product over alumina (activity grade III), employing 5% ether in Skelly B as elutant, gave 0.077 g. (47%) of 4,4'-(α -ketotrimethylene)-1,1',2,2'-bis-(trimethylene)ferrocene (XXI), identified by its infrared, ultraviolet and nuclear magnetic resonance spectra. Recrystallization from hexane gave yellow crystals, m.p. 170-172°.

Anal. Calc'd. for $C_{18}H_{20}FeO$: C, 71.31; H, 6.30; Fe, 17.45.
Found: C, 71.07; H, 6.45; Fe, 17.49.

A portion of the ketone (50 mg.) was reduced with an excess of lithium aluminum hydride - aluminum chloride, as described in previous sections. The product, 1,1',2,2',4,4'-tris-(trimethylene)ferrocene, (XXII) obtained in quantitative yield, melted 145-151°.

Anal. Calc'd. for $C_{18}H_{22}Fe$: C, 74.52; H, 7.25; Fe, 18.24.
Found: C, 74.59; H, 7.34; Fe, 18.43.

Attempted conversion of 2-acetyl-1,1',3,3'-bis-(trimethylene)ferrocene (XXIII) to 1,1',2,2',3,3'-tris-(trimethylene)ferrocene followed methods described in detail above for other acetyl compounds (e.g., II to VIII). Starting material was 0.85 g. (2.75 mmoles) of the 2-acetyl isomer (XXIII), 0.26 g. (5.4 mmoles) of the sodium hydride-mineral oil dispersion (50%), 0.65 g. (5.5 mmoles) of diethyl carbonate. Intermediates from the carbethoxylation, hydrogenolysis and saponification had properties similar to those of the compounds described above. However, when an attempt was made to cyclize the propionic acid intermediate XXV (0.72 g.) with 4.0 ml. of trifluoroacetic anhydride in 20 ml. of carbon tetrachloride the only products obtained were unchanged acid and a compound tentatively identified as β -[1,1',3,3'-bis-(trimethylene)ferrocenyl]-ethyl trifluoromethyl ketone (XXVI). This was shown by its infrared spectrum and by its etching of glass on pyrolysis.

When attempts to cyclize the acid (0.5 g.) with polyphosphoric acid (7 ml.) were made for 2 hours at various temperatures from 0-65° no reaction was observed to take place. As reaction time progressed at 85° increasing amounts of tar with correspondingly decreasing amounts of acid were observed. no neutral material being detected. The crude propionic acid XXV also was converted to its acid chloride by treatment with phosphorus pentachloride, then the acid chloride was treated with aluminum chloride in methylene chloride. The mixture was heated for three hours at reflux, then worked up. The only product obtained was recovered XXV.

Preparation of 1,1'-Trimethyleneferrocene-3,4'-dipropionic Acid (XXXI).

A mixture of 0.400 g. (1.29 mmoles) of 3,4'-diacetyl-1,1'-trimethylene-ferrocene (IV), 5.16 mmoles of sodium hydride, and 0.608 g. (5.16 mmoles) of diethyl carbonate in 250 ml. of sodium-dried benzene was heated for 75 hours at reflux under nitrogen, then cooled, treated with absolute ethanol, and finally with ice and hydrochloric acid. The aqueous layer was extracted with ether and the combined organic phase was washed with water, bicarbonate solution and water, then dried. Removal of solvent on a rotary evaporator yielded 0.83 g. of a wine red oil, the very crude (0.59 g. theoretical) di- β -keto ester contaminated with diethyl carbonate. This oil was hydrogenolyzed in glacial acetic acid over 1.0 g. of platinum oxide at 39 p.s.i., workup yielded 0.48 g. (87% overall) of crude reduced diester as a yellow oil, which was saponified at reflux with 0.1 N sodium hydroxide in ethanol-water (3:2), work-up gave 0.30 g. (72% from diacetyl starting material) of 1,1'-trimethyleneferrocene-3,4'-dipropionic acid (XXXI) m.p. 152-156° dec., whose infrared spectrum contained carbonyl absorption at 1730 cm^{-1} .

Anal. Calc'd. for $\text{C}_{19}\text{H}_{22}\text{FeO}_4$: C, 61.65; H, 5.95.
Found: C, 61.07; H, 6.15.

Cyclization Products from 1,1'-Trimethyleneferrocene-3,4'-dipropionic Acid (XXXI). A mixture of 90 mg. (0.24 mmoles) of the dipropionic acid (XXXI), 75 ml. of carbon tetrachloride, and 1.0 g. of trifluoroacetic anhydride was stirred for 4 hours at room temperature in a tightly stoppered flask, then poured into excess bicarbonate solution. The organic phase was extracted repeatedly with bicarbonate solution, then the combined bicarbonate layers were acidified to pH 4 with hydrochloric acid and extracted with ether. The ether extract was washed with water to pH 5, dried and concentrated to 60 mg. (71%) of a yellow oil, the crude bridged ketone, with infrared carbonyl absorption at 1680, 1720 cm^{-1} . The keto acid was hydrogenated over 50 mg. of platinum oxide at 40 p.s.i. to yield 57.8 mg. (99%) of the crude yellow oily dibridged propionic acid XXVII, whose infrared spectrum had broad carbonyl absorption at 1715 cm^{-1} . A mixture of this oil, 50 ml. of carbon tetrachloride, and 575 mg. of trifluoroacetic anhydride was stirred for 4 hours at room temperature, then poured into excess bicarbonate solution. The aqueous layer was extracted with methylene chloride and the combined organic phases were washed with 1 N potassium hydroxide, with bicarbonate solution and with water to neutrality, then dried and concentrated to 42.1 mg. of an orange oil.

The oil was chromatographed over an acid-washed alumina column, 2.2 x 18 cm. The first fraction was eluted with benzene and yielded 11.3 mg. of a light yellow solid, m.p. 157-161°, whose infrared spectrum was similar to that of 4,4'-ketotrimethylene-1,1',3,3'-bis-(trimethylene)ferrocene (XXVIII), and which was presumably the impure hetero-bridged ketone. The remaining fraction of the column was obtained by extrusion of adsorbent and extraction with chloroform. Removal of chloroform and crystallization from pentane yielded 10 mg. of 4,5- α -ketotrimethylene-1,1',3,3'-bis-(trimethylene)

ferrocene (XXIX), m.p. 163-165°C, whose infrared spectrum was identical with that of the authentic sample obtained above from XXIV.

Acetylation of 1,1',2,2',4,4'-tris-(trimethylene)ferrocene, (XXII) followed the procedure employed for acetylation of VIII. The resulting mixture of 0.166 g. (1.63 mmoles) of acetic anhydride, 0.228 g. (1.63 mmoles) of aluminum chloride and 0.250 g. (0.817 mmoles) of the tribridged compound XXII in 25 ml. of dry methylene chloride was stirred overnight under nitrogen, hydrolyzed with ice water and worked up as usual to give a yellow-brown product, which was chromatographed over alumina (activity III); elution with Skelly B removed 8.1 mg. (3%) of starting material; elution with 1% ether in Skelly B gave 0.234 g. (82%) of 3-acetyl-1,1',2,2',4,4'-tris-(trimethylene)ferrocene (XXXII). Recrystallization from hexane gave yellow-brown crystals, m.p. 119.0-120.0°.

Anal. Calc'd. for $C_{21}H_{24}FeO$: C, 72.42; H, 6.95; Fe, 16.04.
Found: C, 72.54; H, 7.22; Fe, 16.12.

Elution with 20% ether in Skelly B gave 3% of a material of melting point 176-183° and having the composition of a diacetyl-tris-(trimethylene)ferrocene. Its n.m.r. spectrum indicates it to be 3,3'- or 3,5-diacetyl-1,1',2,2',4,4'-tris-(trimethylene)ferrocene.

Anal. Calc'd. for $C_{23}H_{26}FeO_2$: C, 70.78; H, 6.70; Fe, 14.51.
Found: C, 70.23; H, 6.71; Fe, 14.63.

Acetylation of 1,1',3,3',4,5-tris-(trimethylene)ferrocene (XXX) (0.361 g.) was carried out exactly as described above for the acetylations of VIII and XXII; in the present reaction 0.24 g. of acetic anhydride and 0.31 g. of aluminum chloride were employed. Chromatography of the product over alumina (activity III) gave 31.3 mg. (9%) of starting material, eluted with Skelly B. Elution with 1% ether in Skelly B gave 0.177 g. (43%) of a mixture of 2-acetyl- and 2'-acetyl-1,1',3,3',4,5-tris-(trimethylene)ferrocenes accompanied by a small amount of 3-acetyl-1,1',2,2',4,4'-tris-(trimethylene)ferrocene, apparently arising from a small amount of the tris-(trimethylene)ferrocene in the starting material or, more likely, arising from isomerization of the strained fused 5-carbon ring under Friedel-Crafts conditions. Rechromatography over alumina separated the latter compound from the former two; it was eluted more slowly from activity II alumina and was identified by its m.p. 108-112° and its n.m.r. spectrum, identical with that of an authentic sample. The 2- and 2'-acetyl-1,1',2,2',4,5-tris-(trimethylene)ferrocene isomers could not be separated on alumina, however, and they were obtained together as an oil. The n.m.r. spectrum of the oil indicated clearly the presence of two isomers since it would have been uninterpretable for either XXXIII or XXXIV alone. From area ratios of the peaks at 6.62 and 6.34 τ (4:3) it could be shown that the 2-acetyl isomer (XXXIII) was formed in somewhat greater amount. Microanalyses of the mixture were in agreement with the structures.

Anal. Calc'd. for $C_{21}H_{24}FeO$: C, 72.42; H, 6.95; Fe, 16.04.
Found: C, 72.02, 72.51; H, 7.06, 6.93; Fe, 15.93, 16.28.

Elution with 2% ether in Skelly B removed 0.1626 g. (40%) of 4'-acetyl-1,1',3,3',4,5-tris-(trimethylene)ferrocene (XXXV), identified by its spectral properties. Recrystallization from hexane gave 0.14 g. of yellow-brown crystals, m.p. 139.5-142.0°.

Anal. Found: C, 72.36; H, 6.84; Fe, 16.25.

Continued elution with 5% ether in Skelly B, removed another fraction 25.0 mg. (5%), identified as a diacetyl derivative, probably 2,2'-diacetyl- or 2,4'-diacetyl-1,1',3,3',4,5-tris-(trimethylene)ferrocene, m.p. 124-140°, after recrystallization from hexane.

Anal. Calc'd. for $C_{23}H_{26}FeO_2$: C, 70.77; H, 6.71; Fe, 13.98.
Found: C, 70.64; H, 6.76; Fe, 14.57.

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<p>Aeronautical Systems Division, Dir/Materials and Processes, Nonmetallic Materials Lab, Wright-Patterson AFB, Ohio.</p> <p>Rpt. No. WADD TR 61-108 Pt III. SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES FOR USE AS ULTRAVIOLET ABSORBERS. Final Report, Jan 63, 80p. incl illus., tables, 43 refs.</p> <p>Unclassified Report</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> 1. Iron Compounds, ferrocenes 2. Coatings, ultraviolet absorbers I. AFSC Project 7340, Task 734007 II. Contract AF 33(616) 7214 III. Wyandotte Chemicals Corp., Wyandotte, Michigan IV. Schaaf, R. L., K. L. Rinehart, Jr. V. Not avail fr OTS VI. In ASTIA collection 	<p>Aeronautical Systems Division, Dir/Materials and Processes, Nonmetallic Materials Lab, Wright-Patterson AFB, Ohio.</p> <p>Rpt. No. WADD TR 61-108 Pt III. SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES FOR USE AS ULTRAVIOLET ABSORBERS. Final Report, Jan 63, 80p. incl illus., tables, 43 refs.</p> <p>Unclassified Report</p> <p>In a search for metallocene derivatives as additives; monomers, and polymers with high ultraviolet radiation resistance, the preparation of osmocene and ruthenocene analogs of <i>g</i>-hydroxybenzophenone was investigated, and a study was made of the conversion of functional cyclopentadienes to ferrocenes. Urethanes prepared from 1,1'-ferrocenediisocyanate were not unusually stable. New compounds prepared included</p> <p>(over)</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> 1. Iron Compounds, ferrocenes 2. Coatings, ultraviolet absorbers I. AFSC Project 7340, Task 734007 II. Contract AF 33(616) 7214 III. Wyandotte Chemicals Corp., Wyandotte, Michigan IV. Schaaf, R. L., K. L. Rinehart, Jr. V. Not avail fr OTS VI. In ASTIA collection <p>UNCLASSIFIED</p>
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<p>Aeronautical Systems Division, Dir/Materials and Processes, Nonmetallic Materials Lab, Wright-Patterson AFB, Ohio.</p> <p>Rpt. No. WADD TR 61-108 Pt III. SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES FOR USE AS ULTRAVIOLET ABSORBERS. Final Report, Jan 63, 80p. incl illus., tables, 43 refs.</p> <p>Unclassified Report</p> <p>In a search for metallocene derivatives as additives, monomers, and polymers with high ultraviolet radiation resistance, the preparation of osmocene and ruthenocene analogs of <i>g</i>-hydroxybenzophenone was investigated, and a study was made of the conversion of functional cyclopentadienes to ferrocenes. Urethanes prepared from 1,1'-ferrocenediisocyanate were not unusually stable. New compounds prepared included</p> <p>(over)</p>	<p>UNCLASSIFIED</p> <p>1. Iron Compounds, ferrocenes</p> <p>2. Coatings, ultra-violet absorbers</p> <p>I. AFSC Project 7340, Task 734007</p> <p>II. Contract AF 33(616) 7214</p> <p>III. Wyandotte Chemicals Corp., Wyandotte, Michigan</p> <p>IV. Schaaf, R. L., K. L. Rinehart, Jr.</p> <p>V. Not aval fr OTS</p> <p>VI. In ASTIA collection</p> <p>UNCLASSIFIED</p>	<p>Aeronautical Systems Division, Dir/Materials and Processes, Nonmetallic Materials Lab, Wright-Patterson AFB, Ohio.</p> <p>Rpt. No. WADD TR 61-108 Pt III. SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES FOR USE AS ULTRAVIOLET ABSORBERS. Final Report, Jan 63, 80p. incl illus., tables, 43 refs.</p> <p>Unclassified Report</p> <p>In a search for metallocene derivatives as additives, monomers, and polymers with high ultraviolet radiation resistance, the preparation of osmocene and ruthenocene analogs of <i>g</i>-hydroxybenzophenone was investigated, and a study was made of the conversion of functional cyclopentadienes to ferrocenes. Urethanes prepared from 1,1'-ferrocenediisocyanate were not unusually stable. New compounds prepared included</p> <p>(over)</p>	<p>UNCLASSIFIED</p> <p>1. Iron Compounds, ferrocenes</p> <p>2. Coatings, ultra-violet absorbers</p> <p>I. AFSC Project 7340, Task 734007</p> <p>II. Contract AF 33(616) 7214</p> <p>III. Wyandotte Chemicals Corp., Wyandotte, Michigan</p> <p>IV. Schaaf, R. L., K. L. Rinehart, Jr.</p> <p>V. Not aval fr OTS</p> <p>VI. In ASTIA collection</p> <p>UNCLASSIFIED</p>
<p><i>g</i>-hydroxybenzoylosmocene, <i>g</i>-hydroxybenzoylruthenocene, <i>g</i>-methoxybenzoylruthenocene, 1,1'-bis-(<i>β,β</i>-diethoxyethyl)-ferrocene, 1,1'-bis(<i>β</i>-hydroxyethyl)-ferrocene, [(C₂H₅O)₂CHCH₂C₅H₄]₃Fe, (HOCH₂CH₂C₅H₄)₄Fe, dimethyl and diethyl 1,1'-ferrocenedicarbammates, poly(1,1'-ferrocenedimethyl 1,1'-ferrocenedicarbamate), Os₂OCl₈, 6-carbethoxy-3,4-dihydrofulvene, and cyclopentadienes containing <i>β</i>-carbethoxyethyl, cyanomethyl, <i>β,β</i>-diethoxyethyl, and <i>β</i>-hydroxyethyl groups. Isomeric bis- and tris-(trimethylene)ferrocenes were prepared and acetylated. The acetyl products were converted to the propionic acids, which on cyclization gave homoannular ketones as well as the expected heteroannular compounds.</p>	<p>UNCLASSIFIED</p> <p>UNCLASSIFIED</p> <p>UNCLASSIFIED</p>	<p><i>g</i>-hydroxybenzoylosmocene, <i>g</i>-hydroxybenzoylruthenocene, <i>g</i>-methoxybenzoylruthenocene, 1,1'-bis-(<i>β,β</i>-diethoxyethyl)-ferrocene, 1,1'-bis(<i>β</i>-hydroxyethyl)-ferrocene, [(C₂H₅O)₂CHCH₂C₅H₄]₃Fe, (HOCH₂CH₂C₅H₄)₄Fe, dimethyl and diethyl 1,1'-ferrocenedicarbammates, poly(1,1'-ferrocenedimethyl 1,1'-ferrocenedicarbamate), Os₂OCl₈, 6-carbethoxy-3,4-dihydrofulvene, and cyclopentadienes containing <i>β</i>-carbethoxyethyl, cyanomethyl, <i>β,β</i>-diethoxyethyl, and <i>β</i>-hydroxyethyl groups. Isomeric bis- and tris-(trimethylene)ferrocenes were prepared and acetylated. The acetyl products were converted to the propionic acids, which on cyclization gave homoannular ketones as well as the expected heteroannular compounds.</p>	<p>UNCLASSIFIED</p> <p>UNCLASSIFIED</p> <p>UNCLASSIFIED</p>

<p>Aeronautical Systems Division, Dir/Materials and Processes, Nonmetallic Materials Lab, Wright-Patterson AFB, Ohio.</p> <p>Rpt. No. WADD TR 61-108 Pt III. SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES FOR USE AS ULTRAVIOLET ABSORBERS. Final Report, Jan 63, 80p. incl illus., tables, 43 refs.</p>	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> 1. Iron Compounds, ferrocenes 2. Coatings, ultraviolet absorbers 1. AFSC Project 7340, Task 734007 II. Contract AP 33(616) 7214 III. Wyandotte Chemicals Corp., Wyandotte, Michigan IV. Schaeff, R. L., K. L. Rinehart, Jr. V. Not avail fr OTS VI. In ASTIA collection 	<p>UNCLASSIFIED</p> <ol style="list-style-type: none"> 1. Iron Compounds, ferrocenes 2. Coatings, ultraviolet absorbers 1. AFSC Project 7340, Task 734007 II. Contract AP 33(616) 7214 III. Wyandotte Chemicals Corp., Wyandotte, Michigan IV. Schaeff, R. L., K. L. Rinehart, Jr. V. Not avail fr OTS VI. In ASTIA collection
<p>In a search for metallocene derivatives as additives, monomers, and polymers with high ultraviolet radiation resistance, the preparation of osmocene and ruthenocene analogs of g-hydroxybenzophenone was investigated, and a study was made of the conversion of functional cyclopentadienes to ferrocenes. Urethanes prepared from 1,1'-ferrocenediisocyanate were not unusually stable. New compounds prepared included</p> <p>(over)</p>	<p>UNCLASSIFIED</p>	<p>UNCLASSIFIED</p>
<p>g-hydroxybenzoyl osmocene, g-hydroxybenzoyl ruthenocene, g-methoxybenzoyl ruthenocene, 1,1'-bis-(β,β-diethoxyethyl)-ferrocene, 1,1'-bis(β-hydroxyethyl)-ferrocene, $[(C_2H_5O)_2CHCH_2C_5H_4]_3Hf$, $(HOCH_2CH_2C_5H_4)_3Fe$, dimethyl and diethyl 1,1'-ferrocenedicarbamates, poly(1,1'-ferrocenedimethyl 1,1'-ferrocenedicarbamate), Os_2OCl_8, 6-carbethoxy-3,4-dihydrofulvene, and cyclopentadienes containing β-carbethoxyethyl, cyanomethyl, β,β-diethoxyethyl, and β-hydroxyethyl groups. Isomeric bis- and tris-(trimethylene)ferrocenes were prepared and acetylated. The acetyl products were converted to the propionic acids, which on cyclization gave homoannular ketones as well as the expected heteroannular compounds.</p>	<p>UNCLASSIFIED</p>	<p>UNCLASSIFIED</p>
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	<p>UNCLASSIFIED</p>		<p>UNCLASSIFIED</p>

ORGANIC CHEMISTRY

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74 75 76 77 78 79 80

1ST ANALYST EJH
2ND ANALYST TCZ

DATE 6/1
DATE 6/6/63

ALKYL

01 0 ALKANES
1 IC
2 2C
3 3C
4 4C
5 5C
6 6C
7 7C
8 8C
9 9C
10 10C
11 10+C
02 0 TERMINAL
1 NONTERMINAL
2 POLY USAGE

ALKENES

02 0 ALKENES
1 =CH?
2 C=C
3 3C
4 4C
5 5C
6 6C
7 7C
8 8C
9 9C
10 10C
11 10+C
02 12 TERMINAL
03 0 NONTERMINAL
1 POLY
2 POLY USAGE

ALKYNYL

03 0 ALKYNES
1 #C
2 C#C
3 3C
4 4C
5 5C
6 6C
7 6+C
04 0 TERMINAL
1 NONTERMINAL
2 POLY
3 POLY USAGE

ARYL

04 0 BENZENE
1 MONOSUB
2 DISUB
3 TRISUB
4 ORTHO
5 META
6 PARA
7 SYM-TRISUB
8 POLYSUB
9 IND
10 FUSED
11 POLY USAGE

CYCLOALKANES

05 0 CYCLOALKANES
1 3,4M
2 5M
3 6M
4 7+M
5 SAT
6 UNSAT
7 BICYCLO
8 IND
9 FUSED
10 SPIRO
11 POLY USAGE

HALOGENS

06 0 HALOGENS
1 F
2 Cl
3 Br
4 I
5 At
6 POLY USAGE

CARBONYL

07 0 CARBONYL
1 C=O
2 HC=O
3 C=S
4 HC=S
5 O=(RING)
6 S=(RING)
7 MET. CARBONYLS
8 -C-C-
9 POLY USAGE
10 MISC.

COOR

08 0 COOR
1 -COO-ESTER
2 COOH
3 CARBOXY HALIDES
4 F-C=O
5 Cl-C=O
6 Br-C=O
7 I-C=O
8 OCOO
9 -C-O-C-
10 METAL SALT
11 POLY USAGE
12 MISC.

S-COOR

09 0 S-COOR
1 THIO ACIDS (CXXH)
2 S=C-O
3 O=C-S
4 -S-COOH
5 S=C-HALOGEN
6 S=C-Br
7 S=C-Cl
8 S=C-F
9 S=C-I
10 POLY USAGE
11 MISC.

S-HETERO

4863.10 1 S-HETERO
4863.14 2 3,4M
4863.15 3 5M
4863.16 4 6M
4863.17 5 7+M
4863.21 6 O-CONT.
4863.20 7 N-CONT.
4863.22 8 OTHER-CONT.
4863.11 9 IS
4863.12 10 25
4863.19 11 3+S
4863.18 12 IND
4863.24 1 FUSED
4863.23 2 SPIRO
3 POLY USAGE

N-HETERO

3298.10 4 N-HETERO
3298.14 5 3,4M
3298.15 6 5M
3298.16 7 6M
3298.17 8 7+M
3298.20 9 O-CONT.
3298.23 10 S-CONT.
3298.21 11 OTHER-CONT.
3298.11 12 IN
3298.12 1 2N
3298.13 2 3+N
3298.24 3 SALT
3298.19 4 IND
3298.18 5 FUSED
3298.25 6 SPIRO
3298.22 7 POLY USAGE

O-HETERO

3475.10 8 O-HETERO
3475.13 9 3,4M
3475.14 10 5M
3475.15 11 6M
3475.16 12 7+M
3475.19 13 N-CONT.
3475.22 1 S-CONT.
3475.20 2 OTHER-CONT.
3475.11 3 I-O
3475.12 4 2+O
3475.18 5 IND
3475.17 6 FUSED
3475.23 7 SPIRO
3475.21 8 POLY USAGE

N, C

3297.5 11 N,C,S
5090.16 12 =N-C
1398.75 14 0 =N-C
5091.7 1 =N-C
5091.20 2 =S-C
2618.5 3 =N=C
3297.7 4 POLY
3297.6 5 MISC

N, C

3297.2 6 N,C,O
4462.5 7 NC(=)
0785.28 8 =N-
5361.5 9 =N-
0785.75 10 =C(=)
3297.25 11 =N-
1222.5 12 =O-
3297.4 13 POL.
3297.3 14 MISC

C, I

0797.25 3 C,N
1223.5 4 CN
2613.75 5 =N-
0739.2 6 =N-
2150.5 7 =N-
0787.5 8 =N-
0797.75 9 POL
0797.5 10 MISC

OH

2391.6 15 12 OH, SH
2391.4 16 0 OH
2968.25 1 SH
2391.8 2 POL

N, O

3298.27 3 N,O (S)
3291.2 4 =N-
2968.75 5 =N-
3295.5 6 =NO2
3299.75 7 =N-
3299.25 8 =N-
3299.5 9 N-N
3298.29 10 POL
3298.27 11 MISC

S, C

4863.25 17 0 S, O (N)
4860.75 1 O=S
4860.25 2 SO3
4869.5 3 S=C
4860.5 4 SO2
4863.27 5 POL
4863.26 6 MISC

O

3475.26 3475.26
3468.75 3468.75
3567.5 3567.5
5090.10 5090.10
1398.25 1398.25
5257.5 5257.5
3475.28 3475.28
3475.27 3475.27

CHEMISTRY

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6/6/63

S - HETERO	
1863, 10	1 S-HETERO
1863, 14	2 3, 4M
1863, 15	3 5M
1863, 16	4 6M
1863, 17	5 7+M
1863, 21	6 O-CONT.
1863, 20	7 N-CONT.
1863, 22	8 OTHER-CONT.
1863, 11	9 IS
1863, 12	11 2S
1863, 12	10 12 3+S
1863, 19	11 0 IND
1863, 18	1 FUSED
1863, 24	2 SPIRO
1863, 23	3 POLY USAGE

N - HETERO	
298, 10	4 N-HETERO
298, 14	5 3, 4M
298, 15	6 5M
298, 16	7 6M
298, 17	8 7+M
298, 20	9 O-CONT.
298, 23	11 S-CONT.
298, 21	11 12 OTHER-CONT.
298, 11	12 0 IN
298, 12	1 2N
298, 13	2 3+N
298, 24	3 SALT
298, 19	4 IND
298, 18	5 FUSED
298, 25	6 SPIRO
298, 22	7 POLY USAGE

O - HETERO	
475, 10	8 O-HETERO
475, 13	9 3, 4M
475, 14	11 5M
475, 15	12 12 6M
475, 16	13 0 7+M
475, 19	1 N-CONT.
475, 22	2 S-CONT.
475, 20	3 OTHER-CONT.
475, 11	4 I-O
475, 12	5 2+O
475, 18	6 IND
475, 17	7 FUSED
475, 23	8 SPIRO
475, 21	9 POLY USAGE

N, C, S	
3297, 5	11 N,C,S
5090, 16	13 12 =N-C=S
1398, 75	14 0 -N-C(=S)-S
5091, 7	1 =N-C(=S)-NE
5091, 20	2 -S-CN
2618, 5	3 -N=C=S
3297, 7	4 POLY USAGE
3297, 6	5 MISC.

N, C, O	
3297, 2	6 N,C,O
4462, 5	7 NC(=O)-N-N
0785, 25	8 -N-C(=O)-O-
5361, 5	9 =N-C(=O)-N=
0785, 75	11 -C(=O)-N-
3813, 25	14 12 -N=C=O
1222, 5	15 0 -O-CN
3297, 4	1 POLY USAGE
3297, 3	2 MISC.

C, N	
0797, 25	3 C,N
1223, 5	4 CN
2613, 75	5 -N=C
0239, 2	6 -N-C=N
2150, 5	7 -N-C(N)-N-
0787, 5	8 -N=C=N-
0797, 75	9 POLY USAGE
0797, 5	11 MISC.

OH, SH	
2391, 5	15 12 H, SH
2391, 4	16 0 OH
2968, 25	1 SH
2391, 8	2 POLY USAGE

N, O, (S)	
3298, 27	3 N,O (S)
2391, 2	4 =N-OH
2968, 75	5 =N-SH
3298, 5	6 -NO2
3298, 75	7 -N=O
3298, 25	8 -N-N=O
3298, 5	9 N-NO2
3298, 29	11 POLY USAGE
3298, 27	16 12 MISC.

S, O, (N)	
4863, 25	17 0 S, O (N)
4860, 75	1 O=S=O
4860, 25	2 SO3H
4860, 5	3 S=O
4860, 5	4 SO2-N
4863, 27	5 POLY USAGE
4863, 26	6 MISC.

O, S	
3475, 26	7 O,S
3468, 75	8 -O-
3587, 5	9 -O-O-
5090, 10	11 -S-
1398, 25	17 12 -S-S-
5257, 5	18 0 -S-S-S-
3475, 28	1 POLY USAGE
3475, 27	2 MISC.

AMINES	
0239, 5	3 AMINES
3842, 5	4 NH2- (PRI)
4442, 5	5 -NH- (SEC)
5036, 5	6 -N= (TER)
3984, 5	7 -N= (QUAT)
2442, 5	8 =N
0503, 5	9 -N=N-
1329, 5	11 N=N (N=N=)
2359, 5	18 12 -N-N-
5251, 5	19 0 N=N=N-
0501, 5	1 N=N
1883, 4	2 FLUOROAMINES
1883, 8	3 -NF2
1883, 6	4 -NF
1884, 5	5 F2N-NF-
0239, 4	6 SALT (NON-QUAT)
0239, 9	7 POLY USAGE
0239, 7	8 MISC.

PHOSPHORUS	
3634, 2	9 PHOSPHORUS RAD.
3634, 16	11 P=O,S,O
3634, 18	19 12 P=S,2O
3634, 17	20 0 P=O, S, 2O
3634, 19	1 S=PO3
3634, 15	2 S=P-F
3634, 14	3 S=P-F
3634, 11	4 O=P(N) (O)-F
3634, 10	5 O=P, (F), 2N
3634, 13	6 O=P(F) O2
3634, 12	7 O=P-F
3634, 23	8 P,S-(I TO 3S)
3634, 24	9 P,S-(4S)
1224, 75	11 CYCLIC P
3632, 25	20 12 P(+3)
3632, 75	21 0 P(+5)
3617, 5	1 PO4
3634, 21	2 P-MISC.
3634, 25	3 P,S-MISC.
3634, 22	4 POLY USAGE

BORANES	
0687	5
SILANES	
4530	6

MISCELLANEOUS	
22, 23	0 0
	1 1
	2 2
	3 3
	4 4
	5 5
	6 6
	7 7
	8 8
	9 9
	11 11
	12 12

METALS AND METALLOIDS	
2140	24 0 GROUP I
0205	1 ALKALI
0677	2 Ca
1925	3 Fr
2787	4 Li
3806	5 K
4592	6 Na
4365	7 Rb
1134	8 Cu
2102	9 Au
4542	11 As

GROUP II	
2141	24 12 ALKALINE
0208	25 0
0536	1 Ba
0573	2 Be
0780	3 Ca
2845	4 Mg
4110	5 Ra
4821	6 Sn
0785	7 Co
0970	8 Hg
5585	9 Zn

GROUP III	
2142	25 12
0043	26 0 Ac
0232	1 Al
1996	2 Ga
2467	3 In
2707	4 La
4410	5 Sc
5055	6 Tl
5583	7 Y

GROUP IV	
2143	7
2072	8 Ge
2201	9 Hf
2779	11 Pb
5128	26 12 Sn
5139	27 0 Ti
5590	1 Zn

GROUP V	
2144	2
0330	3 Sb
0610	4 Bi
3287	5 N
	6 P
4936	7 Ta
5381	8 V

GROUP VI	
2145	9
0883	11 CHALCOGENS
3781	27 12 Po
4457	28 0 Se
0935	1 Cr
3122	2 Mo
5277	3 W

GROUP VII	
2146	4
5223	5 TRANS. ELEM.
0992	6 Co
2804	7 In
2807	8 Fe
3275	9 Ni
3459	11 Os
3492	28 12 Pt
3744	29 0 Rh
4277	1 Ru
4373	2

2

FRAGMENT RELATIONSHIP!

<div>ALKYL</div> <div>30 0 ARYL 1 CYCLOALKYL 2 HALOGENS 3 CARBONYL 4 COOR 5 S-COOR 6 S-HETERO 7 N-HETERO 8 O-HETERO 9 N,C,S 11 N,C,O 30 12 C,N 31 0 N,O (S) 1 OH, SH 2 S,O (N) 3 O,S 4 AMINES 5 PHOSPHORUS 6 METALS 7 BORANES 8 SILANES 9 MISC.</div>	<div>ALKENYL</div> <div>11 ARYL 31 12 CYCLOALKYL 32 0 HALOGENS 1 CARBONYL 2 COOR 3 S-COOR 4 S-HETERO 5 N-HETERO 6 O-HETERO 7 N,C,S 8 N,C,O 9 C,N 11 N,O (S) 32 12 OH, SH 33 0 S,O (N) 1 O,S 2 AMINES 3 PHOSPHORUS 4 METALS 5 BORANES 6 SILANES 7 MISC.</div>	<div>ALKYNYL</div> <div>8 ARYL 9 CYCLOALKYL 11 HALOGENS 33 12 CARBONYL 34 0 COOR 1 S-COOR 2 S-HETERO 3 N-HETERO 4 O-HETERO 5 N,C,S 6 N,C,O 7 C,N 8 N,O (S) 9 OH, SH 11 S,O (N) 34 12 O,S 35 0 AMINES 1 PHOSPHORUS 2 METALS 3 BORANES 4 SILANES 5 MISC.</div>	<div>ARYL</div> <div>6 ARYL 7 CYCLOALKYL 8 HALOGENS 9 CARBONYL 11 COOR 35 12 S-COOR 36 0 S-HETERO 1 N-HETERO 2 O-HETERO 3 N,C,S 4 N,C,O 5 C,N 6 N,O (S) 7 OH, SH 8 S,O (N) 9 O,S 11 AMINES 36 12 PHOSPHORUS 37 0 METALS 1 BORANES 2 SILANES 3 MISC.</div>	<div>CYCLOALKYL</div> <div>4 CYCLOALKYL 5 HALOGENS 6 CARBONYL 7 COOR 8 S-COOR 9 S-HETERO 11 N-HETERO 37 12 O-HETERO 38 0 N,C,S 1 N,C,O 2 C,N 3 N,O (S) 4 OH, SH 5 S,O (N) 6 O,S 7 AMINES 8 PHOSPHORUS 9 METALS 11 BORANES 38 12 SILANES 39 0 MISC.</div>	<div></div> <div>39 40</div>
<div>S-HETERO</div> <div>44 0 S-HETERO 1 N-HETERO 2 O-HETERO 3 N,C,S 4 N,C,O 5 C,N 6 N,O (S) 7 OH, SH 8 S,O (N) 9 O,S 11 AMINES 44 12 PHOSPHORUS 45 0 METALS 1 BORANES 2 SILANES 3 MISC.</div>	<div>N-HETERO</div> <div>4 N-HETERO 5 O-HETERO 6 N,C,S 7 N,C,O 8 C,N 9 N,O (S) 11 OH, SH 45 12 S,O (N) 46 0 O,S 1 AMINES 2 PHOSPHORUS 3 METALS 4 BORANES 5 SILANES 6 MISC.</div>	<div>O-HETERO</div> <div>7 O-HETERO 8 N,C,S 9 N,C,O 11 C,N 46 12 N,O (S) 47 0 OH, SH 1 S,O (N) 2 O,S 3 AMINES 4 PHOSPHORUS 5 METALS 6 BORANES 7 SILANES 8 MISC.</div>	<div>N,C,S</div> <div>9 N,C,S 11 N,C,O 47 12 C,N 48 0 N,O (S) 1 OH, SH 2 S,O (N) 3 O,S 4 AMINES 5 PHOSPHORUS 6 METALS 7 BORANES 8 SILANES 9 MISC.</div>	<div>N,C,O</div> <div>11 N,C,O 48 12 C,N 49 0 N,O (S) 1 OH, SH 2 S,O (N) 3 O,S 4 AMINES 5 PHOSPHORUS 6 METALS 7 BORANES 8 SILANES 9 MISC.</div>	<div></div> <div>49 50</div>
<div>AD</div> <div><div>4</div><div>0</div><div>3</div><div>9</div><div>2</div><div>9</div></div> <div>74 75 76 77 78 79 80</div>		<div>O,S</div> <div>52 O,S 6 AMINES PHOSPHORUS 7 METALS 8 BORANES 9 SILANES 11 MISC.</div>	<div>AMINES</div> <div>52 12 PHOSPHORUS 53 0 METALS 1 BORANES 2 SILANES 3 MISC.</div>	<div>PHOSPHORUS</div> <div>53 PHOSPHORUS 4 METALS 5 BORANES 6 SILANES 7 MISC.</div>	<div></div> <div>53</div>

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FRAGMENT RELATIONSHIPS

ARYL 1 ARYL 7 CYCLOALKYL 3 HALOGENS 3 CARBONYL 1 COOR 2 S-COOR 0 S-HETERO 1 N-HETERO 2 O-HETERO 3 N,C,S 4 N,C,O 5 C,N 5 N,O (S) 7 OH, SH 3 S,O (N) 0 O,S 1 AMINES 2 PHOSPHORUS 0 METALS 1 BORANES 2 SILANES 3 MISC.	CYCLOALKYL 4 CYCLOALKYL 5 HALOGENS 6 CARBONYL 7 COOR 8 S-COOR 9 S-HETERO 11 N-HETERO 37 12 O-HETERO 38 0 N,C,S 1 N,C,O 2 C,N 3 N,O (S) 4 OH, SH 5 S,O (N) 6 O,S 7 AMINES 8 PHOSPHORUS 9 METALS 11 BORANES 38 12 SILANES 39 0 MISC.	HALOGENS 1 HALOGENS 2 CARBONYL 3 COOR 4 S-COOR 5 S-HETERO 6 N-HETERO 7 O-HETERO 8 N,C,S 9 N,C,O 11 C,N 12 N,O (S) 39 OH, SH 40 0 S,O (N) 1 O,S 2 AMINES 3 PHOSPHORUS 4 METALS 5 BORANES 6 SILANES 7 MISC.	CARBONYL CARBONYL 8 COOR 9 S-COOR 11 S-HETERO 40 12 N-HETERO 41 0 O-HETERO 1 N,C,S 2 N,C,O 3 C,N N,O (S) OH, SH 4 S,O (N) O,S AMINES 5 PHOSPHORUS 6 METALS 7 BORANES 8 SILANES 9 MISC.	COOR 11 COOR 41 12 S-COOR 42 0 S-HETERO 1 N-HETERO 2 O-HETERO 3 N,C,S N,C,O C,N N,O (S) OH, SH S,O (N) 4 O,S 5 AMINES 6 PHOSPHORUS 7 METALS 8 BORANES 9 SILANES 11 MISC.	S-COOR S-COOR 42 12 S-HETERO 43 0 N-HETERO 1 O-HETERO 2 N,C,S 3 N,C,O 4 C,N N,O (S) OH, SH S,O (N) 5 O,S 6 AMINES 7 PHOSPHORUS 8 METALS 9 BORANES 11 SILANES 43 12 MISC.
N,C,S 9 N,C,S 1 N,C,O 2 C,N 0 N,O (S) 1 OH, SH 2 S,O (N) 3 O,S 4 AMINES 5 PHOSPHORUS 6 METALS 7 BORANES 8 SILANES 9 MISC.	N,C,O 11 N,C,O 48 12 C,N 49 0 N,O (S) 1 OH, SH 2 S,O (N) 3 O,S 4 AMINES 5 PHOSPHORUS 6 METALS 7 BORANES 8 SILANES 9 MISC.	C,N 11 C,N 49 12 N,O (S) 50 0 OH, SH 1 S,O (N) 2 O,S 3 AMINES 4 PHOSPHORUS 5 METALS 6 BORANES 7 SILANES 8 MISC.	N,O (S) N,O (S) OH, SH 9 S,O (N) O,S 11 AMINES 50 12 PHOSPHORUS 51 0 METALS 1 BORANES 2 SILANES 3 MISC.	OH, SH 51 4 OH, SH S,O (N) O,S 5 AMINES 6 PHOSPHORUS 7 METALS 8 BORANES 9 SILANES 11 MISC.	S,O (N) S,O (N) 51 12 O,S 52 0 AMINES 1 PHOSPHORUS 2 METALS 3 BORANES 4 SILANES 5 MISC.
AMINES AMINES 12 PHOSPHORUS 0 METALS 1 BORANES 2 SILANES 3 MISC.	PHOSPHORUS 53 PHOSPHORUS 4 METALS 5 BORANES 6 SILANES 7 MISC.	METALS 8 METALS 9 BORANES 11 SILANES 53 12 MISC.	BORANES 54 0 BORANES 1 SILANES 2 MISC.	SILANES 54 3 SILANES 4 MISC.	MISC. 54 5 MISC.

RING INDEX NAME

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cyclopentadiene 15-5

OPEN-ENDED SECTION

COL & ROW

SECTION

2

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4465	6 SEALANTS	5038	4 TEST EQUIPMENT	1031	67 12 COMBUSTION
5053	7 SEMICONDUCTORS		5 OTHERS	1144	68 0 CORROSION
5067	8 TEXTILES			4137	1 REACTION KINETICS
	9 THERMAL INSULATION				② SPECTROGRAPHIC ANALYSIS
	11 OTHERS				3 OTHERS

CHEMICAL IDENTIFIERS

~~Zirconium~~

0-methoxybenzylanthracene

C-h

o-hydroxybenzoic acid (salicylic acid)

Omnia

6 - carbethoxy - 3, 4 - dihydroisoflavone

Days

Belar - carbomethoxyethyl phenylacetate

1, 1, 1,

13. (beta-methylhexyl)-cyclopentadiene

1, 1'

1, 1- bis - (beta - hydroxy ethyl) furan =

3 - 0

1,1-bis (bicyclohexyl) dioctylmethylether-gemischte

11

11. Pinus densata

,

11. In case disagreement

poly (1,1' -biphenyl-4,4' -diyl) functionalized carbon nanotubes

4. 4-methoxybenzoic acid

PROPERTIES			73 0 U			AD			4 0 3 9 2 9			74 75 76 77 78 79 80		
0058	6	ADHESION												
0892	7	CHEMICAL BONDS												
1281	8	CHEMICAL												
1484	9	DENSITY												
1523	11	ELASTICITY												
2864	65 12	ELECTRICAL												
2945	66 0	MAGNETIC												
3116	1	MECHANICAL												
3117	2	MOLECULAR STRUCTURE												
3427	3	MOLECULAR WEIGHT												
3683	4	OPTICAL												
	5	PHOTOSENSITIVITY												
	6	PHYSICAL CONSTANTS												
	7	PHYSICAL												
	8	RADIANT												
4256	9	RESONANCE												
4628	11	SOLUBILITY												
	66 12	STEREO ISOMERISM												
	67 0	STRUCTURAL ISOMERISM												
4891	1	SURFACE												
5024	2	TENSILE												
5082	3	THERMODYNAMICS												
5188	4	TOXICITY												
5445	5	VISCOSITY												
	6	OTHERS												
PROCESSES			CHEMICAL REACTIONS			GENERAL CLASSES OF MATERIALS								
0003	7	ABLATION	0050.5	4	ACYLATION	0210	70 0	ALKALOIDS						
0890	8	CHEMICAL ANALYSIS	0211.1	5	ALKYLATION		1	CELLULOSE COMP.						
0895	9	CHEMICAL EQUILIBRIUM	0831	6	CATALYSIS	0899.5	2	CHELATES						
1023	11	COLORIMETRIC ANALYSIS	1133	7	COPOLYMERIZATION	1054	3	COMPLEX COMP.						
1031	67 12	COMBUSTION	1252	8	DECOMPOSITION	1057	4	COMPOSITES						
1144	68 0	CORROSION	1882	9	FLUORINATION	1224.25	5	CYCLIC METALS						
4137	1	REACTION KINETICS	2213	11	HALOGENATION	1641	6	ENZYMES						
	2	SPECTROGRAPHIC ANALYSIS	2375	68 12	HYDROGENATION	1741	7	FATTY ACIDS						
	3	OTHERS	2381	69 0	HYDROLYSIS	1930	8	FREE RADICALS						
			2590	1	ION EXCHANGE	2324	9	HORMONES						
			2992	2	METALATION	2361.5	11	HYDROCARBONS						
			3291	3	NITRATION	2693	70 12	LAMINATES						
			3463	4	OXIDATION-REDUCTION	3000	71 0	METALORGANICS						
			3636	5	PHOSPHORYLATION	3741	1	PLASTICS						
			3674.5	6	PHOTOLYSIS	1691	2	EXPANDED						
			3786	7	POLYMERIZATION	2253	3	HEAT-RESISTANT						
			4180	8	RECOMBINATION	5086	4	THERMO						
			4858	9	SULFATION	5087	5	THERMOSETTING						
			4930	10	SYNTHESIS	3914	6	PROTEINS						
				69 12	OTHERS	4793	7	STERIODS						
							8	OTHERS						
							9	Elastomers						

CHEMICAL IDENTIFIERS

o-hydroxy-bis-ferrocene
 ferrocene
 Di-aminomethyl-ferrocene
 1,1',3,3'-bis(trimethylene)ferrocene
 1,1',2,2'-bis(trimethylene)ferrocene
 3-acetyl-1,1',2,2'-bis(trimethylene)ferrocene
 1,1',3,3',4,4'-bis(trimethylene)ferrocene
 1,1'-Ferrocene diglyoxylic acid
 bis-ferrocene carboxylic acid

2

Wyandotte Chemicals Corporation

wyandotte • michigan

22 April 1963

ASTIA
ATTN: TIP
Arlington Hall Station
Arlington 12, Virginia

Subject: Final Report No. WADD-TR-61-108, Part III under Contract
No. AF 33(616)-7214

Gentlemen:

The subject report, which is enclosed, is sent to you at the request of Aeronautical Systems Division, Air Force Systems Command.

Any comment or correspondence concerning the material contained in this report should be directed to:

Commander
Aeronautical Systems Division
ATTN: ASRCNE-2
Wright-Patterson Air Force Base, Ohio

Very truly yours,

WYANDOTTE CHEMICALS CORPORATION



C. T. Lenk, Manager
Inorganic Research Laboratories

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Enc.